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HIGH-TEMPERATURE ELECTRICAL PROPERTIES OF INSULATORS AND THEIR COMPATIBILITY WITH REFRACTORY METALS

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by

Richard F. Havell
and
Frederick C. Holtz

prepared for

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SUMMARY REPORT

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HIGH-TEMPERATURE ELECTRICAL PROPERTIES OF INSULATORS AND THEIR COMPATIBILITY WITH REFRACTORY METALS

N65 18933

ABSTRACT

DC resistances of alumina, magnesia, beryllia, and boron nitride were determined in tests between 1100° and 1600°C in nitrogen, hydrogen, and vapors of mercury and cesium. Using the two-probe technique, current measurements were made with tungsten electrodes at voltages between 0 and 180 VDC over periods of a few hours to 100 hours. The mechanical properties and electrical resistance of tungsten, tantalum, molybdenum, TZM, and 90Ta-10W were measured after the metals were heated in contact with the above insulator materials in various atmospheres and vacuum, both with and without an applied DC voltage. These tests were run at elevated temperatures for periods of a few hours to 98 hours.

Author

SUMMARY

Electric propulsion systems for spacecraft will require a knowledge of the high-temperature properties of electrical insulators and refractory metals in contact with the insulators. This program is a two-part investigation to determine the temperature dependence of the resistivity as a function of time and to determine the change in the physical properties of refractory metals due to contact with the ceramic insulators.

The electrical properties were determined from the voltage-current measurements made on the various insulator samples. A two-probe method was used, with polished tungsten electrodes as the probes. The insulators tested--alumina, magnesia, beryllia, and pyrolytic boron nitride--were heated by radiation from an inductively heated tubular susceptor. The test atmospheres were nitrogen, hydrogen, and vapors of mercury and cesium in a carrier gas of hydrogen or nitrogen. Measurements were made with applied voltages between 0 and 90 VDC and at temperatures between 1100° and 1600°C for periods of 100 hours and for short-time cyclic tests.

Electrical resistivity of the insulators tested were, in general, only slightly affected by the test atmosphere. The repeated short-term tests on the same samples gave nearly the same resistivity curve for the data obtained from the cooling cycle measurements. However, the long-time tests on alumina, beryllia, and boron nitride revealed a nonlinear current voltage effect which appears to be dependent on the thermal history of the sample. Some unexplained mechanism appears to block or trap charge carriers above a certain applied voltage. The data from these measurements indicated that the resistivity increases with time. These results were reproducible on different samples of the same material.

Experimental work for establishing the compatibility of various metal-ceramic combinations involved the determination of the change in the mechanical properties and electrical resistance of metal specimens after elevated-temperature contact with the insulators of interest. Unalloyed tungsten, tantalum, and molybdenum, as well as the alloys 90Ta-10W and Mo-0.5Ti-0.08Zr (TZM), were placed in contact with the ceramic materials and heated for as long as 98 hours at 1500°C under various atmospheres. In some cases a DC voltage was applied across the metal-ceramic interface. The metal specimens were evaluated for surface and core hardness, strength, ductile-to-brittle transition behavior, and electrical resistivity.

In general, the Group VI B materials, tungsten, molybdenum, and the molybdenum alloy TZM exhibited very little change in mechanical properties after heating in contact with alumina, beryllia, and magnesia under hydrogen, vacuum, or inert atmosphere at 1500°C. Tungsten specimens exhibited a moderate strength loss after heating in contact with alumina under an applied voltage (90 VDC). All of the Group VI B materials reacted with boron nitride to form very hard surface layers; the formation of these boride layers was suppressed only when the couples were heated with an abundant supply of nitrogen. However, when heated in N_2 the alloy TZM was excessively hardened by internal nitriding of the reactive metal constituents, titanium and zirconium.

Tantalum and the alloy 90Ta-10W were hardened and embrittled after heating in contact with alumina, magnesia, and boron nitride under the various atmospheres. After 98 hours under vacuum at 1500°C, these materials exhibited increases in bend transition temperature to the 600°-1100°C range. Tantalum was hardened by exposure to nitrogen, and even greater surface hardening took place on 90Ta-10W specimens. These materials, like the Group VI B metals, formed very hard boride surface layers after heating in contact with boron nitride. In general, the reduced compatibility of tantalum and the 90Ta-10W alloy was attributed to their high reactivity and high solubility for interstitials such as oxygen and nitrogen.

Of the ceramic materials, alumina appeared to be slightly more compatible with the metals than magnesia; on the basis of short-time tests the metal specimens were little affected by contact with beryllia. Boron nitride reacted with all of the metal specimens except during short-time exposures under flowing nitrogen. Tungsten and molybdenum could be heated in contact with ceramics under hydrogen and nitrogen without deleterious effects, but TZM, tantalum, and 90Ta-10W were embrittled to varying degrees under these atmospheres.

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HIGH-TEMPERATURE ELECTRICAL PROPERTIES OF INSULATORS AND THEIR COMPATIBILITY WITH REFRACTORY METALS

I. INTRODUCTION

Electric propulsion systems for spacecraft will require a knowledge of the high-temperature properties of electrical insulators and refractory metals in contact with the insulators. This program is a two-part investigation to determine the temperature dependence of the resistivity as a function of time and to determine the change in the physical properties of refractory metals due to contact with the ceramic insulators.

The two previous years of investigations(1,2) were concerned with determining the short-time resistivity of selected ceramic insulators at temperatures in the range of 1000° to 1900°C under various atmospheres. The insulators tested were alumina (polycrystalline and sapphire), magnesia, boron nitride (hot pressed and pyrolytic), thoria, beryllia, lava, boron nitride-carbon alloy, and lime-stabilized zirconia; the atmospheres were vacuum, nitrogen, hydrogen ammonia, methane, and vapors of cesium and mercury.

The present investigation, covering the period September 1, 1963, to October 31, 1964, was aimed at determining the effect of long times at elevated temperatures on the electrical properties as well as the effect of repeated cycling of the temperatures. Based on the two prior years' programs alumina, beryllia, boron nitride, and magnesia were chosen to be tested in atmospheres of nitrogen, hydrogen, and vapors of cesium and mercury. Short-term tests of a few hours' duration were made at temperatures between 1100° and 1600°C. The long-term tests were run for 100 hours at temperatures of approximately 1300°C. The applied voltage for these tests was 90 VDC, and the resistivity was determined by a two-probe method.

A second phase to this investigation was initiated this year. It was noted in the previous work(2) that the grain structure of the tungsten electrode was altered when tested at these high temperatures in contact with the ceramic and with an applied DC potential. Hence, it was decided to incorporate a program aimed at determining the change in the mechanical properties and electrical resistance of the refractory metals due to heating in contact with the ceramics in various atmospheres, both with and without an applied DC voltage. The metals investigated included tungsten, tantalum, molybdenum, TZM, and 90Ta-10W; the gaseous environments and insulators were the same as those investigated in the first phase of this program. Both short-term and 98-hour tests were run at 1500°C.

II. ELECTRICAL RESISTANCE OF INSULATORS

The short- and long-term electrical resistance tests of the ceramic samples were made in induction-heated furnaces by the two-probe method using applied potentials that were varied between 90 and 0 VDC. Some supplementary tests were made with potentials as high as 180 VDC. Short-term tests were generally of about 5 to 8 hours' duration, with measurements taken during both heating and cooling cycles. The long-term tests covered periods up to 100 hours with resistance measurements taken only during the daytime, although the equipment operated at test temperatures unattended throughout the night. The test furnaces were essentially fused quartz bell jars surrounded by an induction coil. The sample itself was heated by radiation from tubular graphite, molybdenum, or platinum-rhodium susceptors. Environments within the tube were at approximately atmospheric pressure. Polished tungsten disks were used for electrodes.

A. Equipment and Procedures

1. Sample Preparation and Characterization

Six sample materials were investigated in this program. Of these, two polycrystalline aluminas and magnesia were pressed and sintered at IITRI. Sapphire, pyrolytic boron nitride, and beryllia were obtained from commercial sources.

a. High-Purity Aluminum Oxide

High-purity aluminum (99.999 per cent) was sawed into small pieces about 1 x 1 x 2 inch. After washing, the surface was cleaned by repeatedly dissolving the surface in C.P. hydrochloric acid and washing in distilled water until about 1/8 inch of surface was removed. The remaining metal was then dissolved in HCl, and the resulting aluminum chloride was calcined at 1250°C for 4 hours to thermally decompose it to alpha-alumina powder. The powder was milled in distilled water using polyethylene jars and polystyrene balls. After drying, 12 cc of 1 per cent solution of ammonium alginate was added for each 100 grams of powder, with sufficient distilled water to make a slip. The slip was evaporated to dryness; the powder was placed in a polyethylene bag and mixed in the bag with 7 per cent of distilled water. Rods were hydrostatically pressed (30,000 psi) from this mix and, after drying, were fired to over 1700°C in a Remmey kiln. Densities of the rods ranged from 3.74 to 3.75 g/cc, about 94 per cent of theoretical density.

The fired rods were centerless ground to 0.375 inch diameter and then cut into test lengths. End surfaces were polished by successively lapping with 100 and 150 mesh SiC and on 240, 320, 400, and 600 grit SiC paper. The pieces were then washed in water, methanol, and toluene with drying after each washing. After two rinsings in HCl, the samples were washed in distilled water and redried. Spectrographic analysis (by a commercial laboratory) of a finished sample gave the following impurity levels:

Impurity	ppm
Si	80
Fe	50
Mg	50
B	$<$50 (not detected)
Ca	6
Cr	10
Cu	1
Ni	$<$ 5 (not detected)

b. Alucer Alumina

Alucer MC alumina powder is sold by Gulton Industries. It is reportedly a high-purity material (99.96 per cent) prepared by calcination of alum at approximately 1360°C to give alumina having a particle size of about 1.5 to 2 microns. The supplier gives the following typical analysis:

Impurity	ppm
Si	<50
Fe	< 20
Ti	< 5
Zn	<10
Cr	~50
Pb	70
Ca	10
Cu	2
Na	100

The powder was hydrostatically pressed at 30,000 psi after being slightly moistened with distilled water. After drying, the rods were fired to 1895° and 1910°C in vacuums of about 0.01 to 0.04 microns. Densities of the fired rods ranged from 3.86 to 3.87 g/cc, about 97 per cent of theoretical density.

After the rods were centerless ground to 0.375 inch, samples were prepared in the same manner as for the high-purity alumina. Spectrographic analysis of a finished sample gave the following impurity levels:

Impurity	ppm
Si	300
Fe	200
Mg	200
B	300
Ca	20
Cr	20
Cu	< 1
Ni	< 5 (trace)

The impurities appear to be about four times greater than in the high-purity alumina. The Alucer alumina was tougher than the high-purity samples, and impurities may have been introduced in the preparation for analysis.

c. Sapphire

Samples of sapphire were prepared from 0.375 inch diameter rods received from the Linde Company.

d. Magnesia

Rods of magnesia were prepared from Mallinckrodt AR grade magnesia powder. This material is prepared by decomposing magnesium carbonate at 1400°C and has a particle size of less than 1 micron. The manufacturer reports the following maximum impurity levels:

Impurity	ppm
NH_4OH ppt	200
Ba	50
Ca	500
Heavy metals such as Pb	30
Fe	100
Mn	5
K	50
Na	5000
Sr	50
SiO_2	400

The powder is very fluffy, having a surface area of about 15 m^2/g and a bulk density between 0.1 and 0.2 g/cc. The compaction ratio was reduced by treating the powder with an inorganic binder and lubricant dissolved in an organic solvent.

Four grams of Acryloid B72 and two grams of Dar Chem stearic acid were dissolved in about 150 ml of toluene. Toluene was added to 400 grams of magnesia to make a thick paste to which the dissolved Acryloid and stearic acid was added and mixed. After evaporating the toluene, rods were hydrostatically pressed at 30,000 psi. After sintering to 1750°C in a gas-fired kiln, the rods had densities of 3.51 g/cc (about 98 per cent of theoretical); variation was slight. Test samples were prepared in the same manner as for the alumina samples.

e. Beryllia

Samples of beryllia 0.375 inch diameter by 1/2 and 1/8 inch thick were provided by Brush Beryllium Company. The material was identified as grade F-1 of 99.8 per cent purity. The major component, other than beryllia, was magnesia with very small amounts of other impurities. Densities of the pieces were between 2.94 and 2.95 g/cc, about 98 per cent of theoretical.

f. Pyrolytic Boron Nitride

Disks of pyrolytic boron nitride, 3/8 inch diameter, were cored from small plates of the material contributed by High Temperature Materials, Inc. Prior to coring, the faces of the plates were surface ground to assure parallelism. After forming, the disks were cleaned by lightly abrading all surfaces with 600 grit SiC paper. The samples were tested with electrical conduction in the direction of the "c" axis.

2. Apparatus and Equipment

Two test cells similar to those used in the previous program,(2) were used in this part of the program; one for short-term and other for long-term tests. Basically, the cell consisted of a fused quartz tube about 18 inch long, and equipped with gas-tight joints so as to facilitate evacuation and introduction of gases and vapors. The quartz tube was sealed to a stainless steel baseplate with silicone rubber.

The insulator sample was held between two polished tungsten disk electrodes and was under pressure contact. Two concentric alumina tubes served as radiation shields. A small hole in each of the tubular shields permitted sighting of an optical pyrometer on the test sample. Graphite, molybdenum, and platinum-rhodium susceptors were used. Each of the susceptors had a small hole midway between the ends which lined up with the pyrometer sight holes in the radiation shields.

An induction coil outside the quartz tube was energized by either a Lindberg generator operated at 390 kc or a Lepel generator operated at 420 kc. Sample temperatures were measured with a Leeds and Northrup optical pyrometer sighted between turns of the induction coil and through aligned holes in the radiation shields and susceptor.

Open-circuit voltages across the sample were measured with a Kiethley model, 200A electrometer-type voltmeter. Input impedance of the meter was 10^{14} ohms without a voltage divider and 10^{12} ohms with a 100:1

divider. The potential source for the impressed voltages was dry-cell batteries. The voltage applied to the sample was adjusted by means of three potentiometers. Currents through the sample were measured with a Hewlett Packard Model 425A microvolt ammeter or a Triplett Model 630-NS volt-ohm-milliammeter. Applied voltages were measured with the electrometer, a Triplett 630-NS, or a Simpson Model 206 voltmeter. The electrometer was placed in the circuit between the sample and the current meter; the other voltmeters were used with the current meter between them and the sample.

Two low-pass filters were placed in the leads between the meters and the sample to remove RF from the lines. One filter was near the furnace and the other next to the meters.

3. Testing Procedures

a. Electrical Measurements

All of the resistivity measurements were made by the two-probe method in which the electrodes at the ends of the sample are the two probes. Various DC voltages were applied to the electrodes, and the current flowing through the sample at these voltages was measured while the sample was held at a constant temperature. During the short-term cycling tests, measurements were made during both the heating and cooling cycles. Generally, the voltage was varied in steps from 90 to 0 to 90 VDC. However, some tests were made with the sample on open circuit between each series of measurements. In these cases the voltage was varied from 0 to maximum to 0 volts. The maximum voltage was from 90 to 180 VDC. The apparent resistance of the sample is inversely proportional to the slope of the current vs. voltage curve where voltage is plotted as the abscissa, or:

$$R = \frac{\Delta E}{\Delta I}$$

where R = resistance, ΔE = change in voltage, and ΔI = change in current. The resistivity can be calculated from the formula:

$$\rho = R\frac{A}{L}$$

where ρ = resistivity in ohm-cm, A = cross sectional area in cm^2, and L = length between probes in cm.

b. Atmospheres

After the sample was set in place and the furnace assembled, the furnace was evacuated and then filled with nitrogen or hydrogen. This purging was repeated an additional two or more times, after which the gas was permitted to flow slowly through the furnace before and while the sample was being heated.

Prepurified nitrogen containing a small amount of hydrogen, or hydrogen containing 50 per cent argon were passed through a palladium catalyst to react any oxygen with hydrogen. A drying train consisting of Drierite, Molecular Sieve, and a cold trap followed the catalyst. Initially, the nitrogen gas was cold-trapped in liquid nitrogen and the hydrogen-argon in liquid oxygen. Oxygen was used in the latter case instead of liquid nitrogen so that the argon would not freeze. The argon was used to lower the thermal conductivity of the test gas. Liquid oxygen was found to be satisfactory for trapping the nitrogen gas and in latter tests was used exclusively for trapping.

Cesium and mercury vapors were introduced to the furnace from a boiler attached to the side wall inlet near the bottom of the quartz tube. A carrier gas, either nitrogen or hydrogen-argon, was introduced at the boiler, and a small flow was maintained during the test. Infrared lamps and electric heating tapes were used to heat the glassware and baseplate to a temperature higher than that of the vapor boiler.

B. Data and Results

The data in this section are divided into a discussion of the tests on the various ceramics. The effect of the atmosphere is given for each ceramic, as well as the results of the long- and short-term tests. For convenience, resistivity and current vs. voltage curves, Figures 1 through 63, are grouped at the end of the report. In the curves, resistivity (ohm-cm) is plotted logarithmically on the ordinate, and the reciprocal of absolute temperature is on the abscissa.

1. Alumina

a. Nitrogen Environment

High-purity alumina specimens, 1/2 inch thick, were tested using a graphite as well as a platinum susceptor. Resistance measurements were made at 90 VDC during the heating and cooling cycles of a series of tests run on separate days. The atmosphere for these tests was prepurified nitrogen and prepurified nitrogen containing 1000 ppm of hydrogen. Between tests, the sample and the furnace were not disturbed.

A summary of the heating and cooling cycle curves has been obtained, and is shown in Figure 1. The cooling cycle curves are shown in Figure 2. The heating cycle curves in Figure 1 are very close to those obtained earlier on a test of the same size sample under similar conditions but heated to a higher temperature.(2) Below 1400°C the resistivity is quite low, probably as a result of impurity charge carriers. Between 1200° and 1500°C the current vs. voltage curves at various test points were erratic, and the resistivity curve is represented by a dashed line. Succeeding tests made to 1630°, 1680°, and 1710°C gave heating cycle resistivity curves which tended to lie along the cooling cycle curve of the preceding test. In each case, the cooling cycle curve is a little below the heating cycle curve for the same test, which would indicate increased contamination at high-temperatures during each test.

Another sample of high-purity alumina, 1/2 inch thick, was tested using a platinum susceptor. Resistance measurements were made at 90 VDC during the heating and cooling cycles of a series of four tests run on separate days; the atmosphere was prepurified nitrogen containing 1000 ppm of hydrogen. Between tests, the sample and the furnace were not disturbed. Results of the individual tests are shown in Figure 3. A summary of the cooling cycle curves are shown in Figure 4. In the first test the DC voltage was not applied to the sample until it reached 1200°C. The increase in resistivity of the sample over a period of 50 minutes at 1200°C is shown in Figure 3. Between 1300° and 1500°C there was a marked improvement in resistivity, presumably as impurity charge carriers were depleted.

After cooling, three additional tests were made on successive days with the polarity of the applied voltage being reversed for the last test. Heating cycle curves for the last three tests were all higher than that for the first test, which would suggest that at least some of the impurity charge carriers had been volatilized during the first test. During the fourth test, the drop in the heating cycle resistivity curve at 1300°C may be due to impurity carriers that were not volatilized and had started to migrate at this temperature. In contrast to the tests made with a graphite susceptor where the cooling cycle curves dropped slightly in each successive test, all four curves with the platinum susceptor tended to coincide. Since the tests were conducted on like samples in a similar manner, it appears that vapors from the graphite susceptor tended to slightly lower the resistance of the alumina in the successive tests. Weight change by the alumina after the four tests with the platinum susceptor was 0.9 mg gain, about 0.03 per cent.

The first 100-hour test was made on a 1/2 inch thick sample of the high-purity alumina in nitrogen, using a platinum susceptor. Difficulty with the liquid nitrogen transfer equipment resulted in oxidation of tungsten parts when the cold trap warmed overnight and permitted the previously trapped moisture to enter the furnace. The trap design was altered, and the transfer difficulties were corrected during the test. Additional tungsten oxidation occurred during the switch of cold trap equipment, and the test was concluded after four days. Resistivities during the heating cycle were similar to those in Figure 3. The sample was held at 1300°C, and the resistivity started to increase but fell to lower values after oxidation of the tungsten occurred. The sample had an increase in weight of 4.3 mg, about 0.12 per cent.

Results of a second 100-hour test of a 1/2 inch thick sample of high-purity alumina tested to 1300°C with a platinum susceptor in prepurified nitrogen containing 1000 ppm of hydrogen are shown in Figure 5. Weight change of the alumina was negligible, a loss of 0.1 mg. During the heating cycle, plots of current vs. voltage between 90 and 0 volts were linear and passed through the origin. Four hours after the start of the test, at 1290°C (1 1/4 hours after the readings taken at 1320°C), the current vs. voltage plot was still linear and through the origin, although the resistivity was higher than it was at 1275°C on the heating cycle. Current at 90 volts was 45 1/2 microamperes. At 5 1/2 hours the current (again at 1290°C) had dropped to 20 microamperes at 90 volts. The current vs. voltage plot was no longer linear from 90 to 0 volts (Figure 6a). Upon lowering the voltage from 90 to 85, there was no change in current and, as the voltage was further lowered, the current increased to a maximum and then fell off. Below 70 volts the plot was on a straight line passing through the origin. By 7 1/2 hours, the flat portion of the curve below 90 volts had lengthened; the maximum current was observed at 55 volts. Between 90 and 65 volts the current varied from 19 to 20 microamperes. In Figure 5, the indicated resistivities were calculated from the slope of the straight portion of the curve which passed through the origin for all readings from the fourth hour of the test on. After 24 hours, the straight line generally started between 40 and 35 volts and extended to 0 volts. Figure 6b, 6c, and 6d illustrate the shape of the curves after 24, 49, and 96 hours of testing. Similar current curves were obtained during the cooling cycle until 1095°C when the linear portion of the curve, which had become very short, no longer passed through the origin, Figure 7a. At 1050°C, Figure 7b, there was no longer any linear portion of the curve.

Another 1/2 inch thick sample of high-purity alumina was tested to 1500°C with a platinum susceptor in prepurified nitrogen containing 1000 ppm of hydrogen. Results of this 100-hour test are shown in Figure 8. During the test the resistivity at 1500°C increased nearly two orders of magnitude, apparently as a result of the depletion of impurity charge carriers by volatilization and migration. On the fourth day of the test, the temperature took a rapid excursion to room temperature during a power failure. After the power was restored, the sample was reheated and the test continued.

During the initial heating cycle, at 1400°C the current vs. voltage curve started to sag at the upper voltages in a manner similar to that of the curve in Figure 6a. At 1450°C the straight-line portion of the curve lies between 40 and 0 volts. The hump between 40 and 60 volts was not so pronounced as in Figure 6c. After the first day, the current vs. voltage curves tended to be linear at the higher voltages with a slope such that, if extrapolated, the curve would pass near the origin. At lower voltages varying from 20 to 40 volts, there was a rapid decrease in current as the voltage was lowered. Weight loss by the sample was only 0.1 mg.

A 1/2 inch thick sample of high-purity alumina was heated to 1300°C in nitrogen with the measuring circuit open and no voltage applied to the sample until it had been at temperature for about 1 hour. Current measurements were made by varying the applied voltage from 0 to 90 volts and back to 0 volts. All points fell on a straight line, and the resistivity was 6.6×10^5 ohm-cm at 1295°C (Figure 9), which is slightly lower than the 8×10^5 ohm-cm of the previously tested sample (Figure 5), which had been heated with a potential of 90 volts applied to the sample. For the next 3 1/2 hours straight-line current vs. voltage curves were obtained. Between measurements the sample was left at temperature without an applied voltage. After 24 hours from the start of the test, there was a small break in the current vs.voltage curve (Figure 10) at 60 volts and a drop in current at 70 volts. The shape of the curve obtained as the voltage was reduced was similar to that obtained previously when 90 volts were left on the sample between measurements, and measurements were made from 90 to 0 volts. There was a slight improvement in resistivity during the next 24 hours of the test. For the remainder of this time the current vs. voltage curves showed little change. An applied potential of 90 volts was left on the sample for the next 12 hours. However, the current at a given voltage is larger in the present test than in the previous one after the same amount of time.

Figure 11 shows the current-voltage curve after 48 hours. The point where the current drops has moved toward the left, and the resistivity has increased; there was little change during the next 12 hours. After 76 hours, there was evidence of some oxidation during the night and the current-voltage curve was linear. The sample was cooled, and the curves remained linear.

Another 1/2 inch thick sample of high-purity alumina was heated in nitrogen. Resistivity results are shown in Figure 12. After 4 hours (1 hour at 1290°C) voltage was applied to the sample. In order to see if there was a current drop at some voltage higher than previously used, measurements were continued beyond 90 volts. At 140 volts, there was a small current drop, and at 150 volts a large drop. The current vs. voltage curve is shown in Figure 13. As the voltage was reduced from 180 volts, the current remained fairly constant until 100 volts. Two hours later, voltages were reapplied at 1330°C. The drop in current occurred at 130 volts with an increasing voltage. Current was again fairly constant from 180 to 110 volts where it increased as the voltage was being lowered. From 100 to 0 volts the curve was linear to the origin. The sample was left without an applied voltage overnight and between all of the measurements in the next 24 hours as the sample was cooled. Figure 14 shows the current vs.voltage curve after 24 hours. The curve now breaks from linearity at 70 volts, and the current remains fairly constant. As the temperature was lowered, the break in the current vs. voltage curve moved toward lower voltages. The curve obtained at 1095°C (28 hours from start of experiment) is shown in Figure 15. The portion of the curve obtained when the voltage was reduced from 90 to 0 volts is very similar to a curve previously obtained at the same temperature after almost 100 hours of testing (Figure 6d) although currents are almost an order of magnitude larger in the present test.

Another 1/2 inch thick sample was heat-treated prior to testing in nitrogen. It was heated in air using a platinum susceptor. After 1/2 hour at 1575°C the sample was air quenched. Resistivities calculated from resistance measurements are shown in Figure 16. The sample was heated with the measuring circuit open for 4 hours (2 hours at 1295°C). Figure 17 shows the current vs. voltage curve obtained when voltages were applied. The drop in current at 40 volts contrasts strongly with the curve in Figure 13, where the large drop occurred at 150 volts obtained from a similar test on an unquenched sample. There was little change in the current-voltage curves through 24 hours of testing except for a slight improvement in resistivity. On cooling, the break in the curve worked over to 20 volts.

A 1/2 inch thick sample of sapphire was tested in nitrogen-2 per cent hydrogen in order to obtain current vs. voltage curves for comparison with those obtained from high-purity polycrystalline alumina. The sapphire was heated to test temperatures without an applied voltage. Under these conditions an intrinsic voltage was set up in the sample. This voltage will be hitherto referred to as the "open-circuit emf." The cause of this is as yet not known. These voltages were less than 6 volts up to 1200°C. At 1260°C the open-circuit emf had increased to 135 volts, and at 1285°C it was 150 volts. The furnace was cooled and opened to see if anything had happened to the setting of the sample which might account for the large voltages. The samples and setting were normal, and after resetting the sample was reheated on the following day. Open-circuit emf's were less than 2 volts up to 1075°C but increased rapidly at higher temperatures, reaching 45 volts at 1105°C and 220 volts at 1200°C. At 1305°C the voltage dropped to 140 volts. After 1 1/2 hours at this temperature the voltage had dropped to 104 volts.

Resistivities calculated from the resistance measurements are shown in Figure 18. After the sapphire had been at approximately 1300°C for 1 1/2 hours (4 hours from the start of heating), voltages were applied to the sample. The current vs. voltage curve obtained from the initial test at 1290°C is shown in Figure 19. Unlike the high-purity alumina, the sapphire did not show any drop in current at the higher voltages. At 180 volts the sapphire showed an increase in current that was not observed in any of the later measurements. Between tests the sample was left on open circuit. During the next 24 hours the maximum currents were a bit lower, the current vs. voltage curves were a bit straighter, and the increasing and decreasing voltage curves were closer although the decreasing curve was still above the increasing curve. After 72 hours, the currents were much smaller at 1295°C. As the temperature was reduced, the current vs. voltage curve for decreasing voltage first fell on the increasing voltage curve and then slightly below it as the temperature was further reduced.

Three short-term tests were made in nitrogen on one sample of Alucer alumina. The results are shown in Figure 20. The 1/2 inch thick sample was first heated with a platinum susceptor. In the first test, the sample lost 0.5 mg. After resetting, the sample was heated with a new molybdenum susceptor. Two additional tests were made, the results of which are also shown in Figure 20. The resistivity of the Alucer alumina appeared to be poorer than when tested with the platinum susceptor. This may be the result of the deposition of a metallic-appearing, highly conductive coating on the lateral surface of the sample. The coating did not extend entirely to either end surface. An X-ray analysis of a fuzzy deposit around the top of the susceptor revealed that it was molybdenum. The sample gained 1.6 mg in weight.

Results of a 100-hour resistivity test on a 1/8 inch thick disk of Alucer alumina in nitrogen-10 per cent hydrogen are shown in Figure 21.

A second sample of Alucer alumina, 1/2 inch thick, was tested in nitrogen containing 1 per cent hydrogen. Results of these tests, carried out every 24 hours and terminated after a total time period of 72 hours, are shown in Figure 22.

The resistivity of the sample increased between 48 and 72 hours of testing, but after that time period it dropped, and the test was discontinued. There was some evidence of oxidation of the tungsten parts.

A 1/2 inch sample of Alucer alumina heated in nitrogen-2 per cent hydrogen without an applied voltage, developed an open-circuit emf that increased from 2 volts at 1120° to 157 volts at 1235°C. At 1280°C it fell from 126 to 55 volts in 2 hours. Figure 23 shows the current vs. voltage curve obtained when voltages were then applied to the sample. This curve is similar to many of the curves obtained from the high-purity alumina in that after attaining a maximum current as the voltage is increased, the current then decreases with further increase in voltage. Between measurements the sample was left without an applied voltage. Three hours after the curve recorded in Figure 23 was obtained, the drop in current was less, following the maximum as the voltage was raised; on lowering the voltage, the curve crossed the increasing voltage curve as in Figure 24, which was obtained 27 hours after that shown in Figure 23. Similar curves were obtained until the sample was cooled after 72 hours. Maximum currents decreased during the successive tests until after 48 hours the maximum was about 9 microamperes at 50 volts.

During the cooling cycle, the current vs. voltage curves resembled those in Figure 23, although from 0 to 30 or 40 volts the curves were linear. The difference in slope of this portion of the curve and of the decreasing voltage curves would give resistivities differing by an order of magnitude.

b. Hydrogen Environment

Results of a 100-hour test of a 1/2 inch thick sample of high-purity alumina tested to 1200°C in an atmosphere of hydrogen and argon are shown in Figure 25. The sample was heated by a platinum susceptor; weight loss was 0.3 mg.

During the first 4 hours the current vs. voltage curves were linear and passed through or near the origin, until about the fifth hour. After the fifth hour, the curve was linear but intersected the abscissa from 24 to 34 volts. During the next 24 hours the curves were still linear and intersected the abscissa between 25 and 30 volts. After 72 hours, the curves started to drop at the higher voltages, but below 70 volts they were still linear and were intersecting the abscissa at 10 volts. After 96 hours the curves were linear below 40 volts and passed through the origin. Between 90 and 40 volts, there was very little change in current with change in voltage. This shape of the curve was accentuated after 120 hours of testing and was quite flat from 90 to 30 volts; below this point the curve was linear and passed through the origin.

A short-term test in hydrogen-argon was made on a 1/2 inch thick sample of high-purity alumina. The sample was heated with a graphite susceptor to 1500°C. Results are shown in Figure 26. All of the current-voltage curves were linear but intersected the abscissa and the ordinate at various points near the origin. After cooling, the undisturbed sample was reheated on the following day without a potential being applied to the electrodes. Figure 27 is a plot of the open-circuit emf measured on the heating and cooling cycle with an electrometer. The positive and negative voltages are in respect to the polarity of the applied voltages in the previous test. These voltages are possibly the result of rectification of the RF field by the sample since in one of the subsequent tests, the voltage collapsed when the generator was turned off with the sample at 1500°C. The peculiar shapes of the heating and cooling curves may reflect the influence of prior testing with an applied voltage since the curves were reproduced in subsequent tests and do not appear to be random wanderings.

The test was repeated, and the open-circuit emf's for both the heating and cooling cycles were virtually the same as those observed in the previous test. In a fourth test, the sample was heated without an applied voltage, and again the open-circuit emf curve nearly duplicated that from the two previous tests. At 1540°C, 90 VDC was applied and resistances were measured as the sample was cooled. The cooling cycle curve of this final test is shown in Figure 26. The shape and slope of this curve are nearly the same as those of the cooling cycle curve for the first test, but the resistivity values are about one-half to one-third as large as those observed originally. Lowering of the resistivity is presumably the result of reactions due to the presence of vapors from the graphite susceptor. The sample lost 18.4 mg (about 0.6 per cent) in the four tests. The tungsten rod leading to the top electrode was covered with white whiskers above the hot zone; the lateral surface of the sample had a thin, white fragile shell. Similar whiskers and shells were observed after tests on alumina and sapphire made in a previous program under like conditions. X-ray diffraction analyses were made on the whiskers and shell obtained in the present test using powder cameras. The shell gave a strong AlN pattern with a trace of alpha-alumina. The whiskers gave patterns of gamma-alumina, a trace of alpha-alumina, and a strong pattern from an unidentified phase(s). The reason for the AlN pattern from the shell on the sample is unknown. The hydrogen in the furnace was flushed with nitrogen, but only after the sample was cold. The formation of an AlN shell has not been observed after tests on alumina in nitrogen below 1500°C with either platinum or a graphite susceptor.

Two 100-hour tests were made on one sample of high-purity alumina, 3/8 inch diameter by 1/2 inch thick; both tests were made in hydrogen-argon. Results of the first test to 1200°C using a tantalum susceptor are shown in Figure 28. The sample had a negligible weight change, a loss of only 0.1 mg. The sample was reset using the same electrodes and, using a molybdenum susceptor, tested to 1300°C. Results of this test are shown in Figure 29. There was no further change in the weight of the high-purity alumina as a result of the second test.

In the first test, the tantalum susceptor was used. The current vs. voltage curves were quite linear for the first 4 hours after which, below 30 volts, the current fell off rapidly. During the next 24 hours (second day) the current fell off rapidly below 40 to 45 volts. After 48 hours (third day) the curves were linear at the higher voltages, above about 60 volts, and curved with rapid fall-off of current below 60 volts. This same type of curve was observed on the last day of the test before the temperature was reduced. As the temperature was lowered, the curves tended to improve and become linear for their entire range.

In the second test of this sample (above about 1200°C), a strong voltage on the sample resulted in negative currents. These could be due to impurities that form p-n type junctions within the test specimen at elevated temperatures. The negative currents persisted for the first 72 hours of the test, when they gradually lessened, and on the 79th hour, a good current vs. voltage curve was obtained. After 96 hours, linear current vs. voltage curves were obtained; however, only at 1315° and 1080°C were the currents positive. The points on the curve at 1255° and 1190°C are of doubtful accuracy since they were calculated from the slopes of lines in which all of the current values were negative.

A 1/2 inch thick sample of sapphire was tested in hydrogen-argon for 100 hours. There was no improvement in the resistivity at the maximum temperature after the first 24 hours. Results of the test are shown in Figure 30. The sample appeared to be unaffected by the test; weight loss by the sapphire was approximately 0.1 mg.

A sample of Alucer alumina, 1/2 inch thick, was tested for 100 hours in hydrogen argon. The resistivity curve obtained while the sample was cooled at the end of the test coincides down to 1100°C with the curve obtained from sapphire (Figure 30). The resistivity of the Alucer increased almost an order of magnitude between 12 and 24 hours; after that there was little improvement. Resistivities are shown in Figure 31. Current vs. voltage curves were variable and rarely linear at any temperature; weight loss by the sample was 0.4 mg.

Three short-term tests in hydrogen-argon were made on one sample of 1/2 inch thick Alucer alumina. The sample was reset, with the same electrodes, between the second and third tests. Resistivity results obtained from cooling cycle curves are shown in Figure 32. In the first test, 90 VDC was applied to the sample at 1050°C, and a current of about 40 microamperes flowed through the sample. After 4 minutes the current dropped to less than 4 microamperes. As the temperature was increased, the current became negative until 1230°C. Again, as the temperature was raised, the current was negative and remained so up to 1320°C and down to 1285°C. From 1285°C down, currents were positive. When retested, currents were unsteady at 1285°C and became negative between that temperature and 1400°C, although to a lesser extent than in the first test. The resistivity curve obtained in these three tests was almost identical to the cooling curve for sapphire (Figure 30).

The sample was removed from the furnace and reset before the third test. Apparently it acquired some impurities during the process, since the heating cycle resistivity curve was far below the cooling cycle curve below 1300°C. Above this temperature, the curves coincide. Surprisingly, the current remained normal up to 1400°C with no negative currents as seen in the first two tests. Resetting appears to have disrupted whatever was causing that effect. The cooling cycle resistivity curve lies between those obtained in the first two tests.

Another 1/2 inch thick sample of Alucer alumina was tested for 100 hours in hydrogen-argon. Results of this test are shown in Figure 33.

During the first 24 hours of testing, a transition occurred at 1255°C where current through the ammeter switched from all positive values to all negative values. Later, the transition to all negative currents occurred at about 1275°C, whereas the return to all positive currents occurred at about 1210°C. After 48 hours of testing, the transition temperatures were 1245° and 1210°C and remained at these values through the next 48 hours (fifth and sixth days) of the test. There was no weight change in the sample during testing.

Another 1/2 inch thick sample of Alucer alumina was heated in hydrogen-argon to 1200°C. Currents, with 90 volts applied, remained small and positive without any reversals of current through the next 24 hours (second day). At temperatures between 1200° and 1235°C the currents at 90 volts were less than 10 microamperes. During the next 48 hours (third day) currents remained positive and at 90 volts varied from 2.9 microamperes at 1215°C to 80 microamperes at 1255°C. After 72 hours (fourth day) at 1295°C there was a large negative current of 240 microamperes at 90 volts and 340 microamperes at 0 volts. When the high-frequency generator was shut off, the negative current collapsed and did not reappear when the power was reapplied. Instead, a large positive current of 600 microamperes was observed. The current remained abnormally large as the sample was cooled to 1210°C. At 1165°C the current fluctuated between 5 and 30 microamperes with 90 volts applied potential. At 1150°C the current was steady at 1.4 microamperes.

c. Mercury Vapor Environment

Four short-term resistivity tests were made on a 1/8 inch thick sample of Alucer alumina in mercury vapor with a hydrogen-argon carrier. Results of the first two tests are shown in Figure 34; the data from the last two tests appeared to be too erratic for calculating resistivities.

In the first short-term tests there was a sharp fall-off in current when the applied potential was lowered below 10 volts as the sample was heated up to 1120°C, while above this temperature the fall-off was markedly reduced. During the cooling cycle, the I vs. E curve was erratic at 1230°C, and at lower temperatures it was linear from 90 to 30 volts where the current tended to fall more quickly, but much less than during the heating cycle. In the second test, the points on the curve started to scatter. In both the third and the fourth tests, the currents were unsteady, and strong rectified voltages were observed between 1150° and 1250°C.

A similar 1/8 inch thick piece of Alucer was tested for 100 hours in mercury vapor with a hydrogen-argon carrier. During the heating cycle, there was a power failure at 1055°C and the sample was then reheated. Resistivity results are shown in Figure 35. During the first 24 hours of testing at 1210°C and 90 volts potential difference there was a sudden increase of current, which was an order of magnitude larger. Both before and after the increase, currents were in a positive direction. The change occurred while current and voltage readings were being made, and the vertical line of the heating cycle curve connects the values of the resistivities before and after the increase in current. Currents after the change were unsteady, and the resistivity value plotted may be too small since the next two resistivity values obtained 15 and 75 minutes later were calculated from steady current conditions.

After 24 hours of testing there was too much scatter in current vs. voltage plots, and no resistivities were calculated. A transition temperature existed between 1175° and 1195°C, at which temperature the current through the ammeter would switch from small currents, all in a positive direction, below the transition to larger (about two to three orders of magnitude) currents all in a negative direction above the transition temperature. After 48 hours, the resistivity measurements were made below the transition temperature. By 72 hours, the switch to all-positive from all-negative currents would occur at about 1150°C, while the reversal to all-negative currents would occur at about 1195°C. The sample did not change weight during testing.

d. Cesium Vapor Environment

Resistivities obtained for a 1/2 inch thick sample of Alucer alumina tested for 100 hours in cesium vapor with a hydrogen-argon carrier are shown in Figure 36. The resistivity of the sample at 1300°C increased about one order of magnitude during the test. Current vs. voltage plots were generally linear after the first 24 hours until the temperature was reduced at the end of the test when the tendency was for a more rapid change of current below rather than above 20 volts.

Results of two short-term tests on a 1/2 inch thick sample of Alucer alumina in cesium vapor with a prepurified nitrogen carrier are shown in Figure 37. The cooling curve is parallel to and just below the curve obtained after 100 hours in cesium vapor.

2. Magnesia

a. Nitrogen Environment

A 100-hour test on magnesia in nitrogen resulted in considerable reaction between the insulator and electrodes. The 0.375 inch diameter of the 1/2 inch thick sample increased during the test. At the anode end, it was 0.380 inch; at the cathode end, it was 0.400 inch. The length increased by 0.008 inch, and the weight increase was 133 mg. A metallic-appearing scale adhered to the anode end of the sample. X-ray diffraction analysis of the end surfaces showed other compounds besides magnesia to be present. The unidentified patterns are strong, and different patterns were obtained from the two surfaces. Resistivity results are shown in Figure 38.

Figure 39 shows the results of two short-term tests in nitrogen on a 1/2 inch thick sample of magnesia. Weight gain by the sample totaled 1.0 mg. Most of the current vs. voltage curves were nonlinear above 1200°C. Generally, the current showed little change as voltage was varied at the higher and middle ranges of voltage. Some of the curves showed peak currents for the middle range voltages. Currents fell rapidly as the voltage was reduced below 20 volts. X-ray analysis of the end surfaces gave different patterns; however, both contained MgO. Neither pattern was similar to either pattern obtained from the 100-hour test sample above.

Resistivity results for a 100-hour test of a 1/2 inch thick sample of magnesia in N_2-$2H_2$ are shown in Figure 40. Two power failures occurred during the heating cycle. Weight loss during testing amounted to 2.3 mg (about 0.08 per cent).

Except for the second and third heating cycles during the first 24 hours, the I vs. E curves were linear and intersected the axis at or very close to the origin. During the second and third heating cycles the curves tended to flatten at the higher voltages where the rate of change in current was slight with voltage change.

b. Hydrogen Environment

A 1/2 inch thick sample of magnesia was tested in hydrogen-argon for 100 hours at about 1300°C. Results of this test are shown in Figure 41. For two days the linear plots of current vs. voltage passed through the origin. On the third day, a voltage of the same polarity as the applied voltage developed across the sample and persisted until the temperature was lowered on the fifth and final day of the test. Weight loss by the sample was 2.7 mg (0.09 per cent). X-ray diffractometer analysis of the sample's two end surfaces showed only peaks from magnesia.

The resistivity curve of another 1/2 inch thick sample of magnesia (Figure 42), after three short-term tests, was approaching the curve obtained in Figure 41 after 100 hours.

A long-term test was started on a 1/2 inch long sample of magnesia in hydrogen-argon. The sample was heated with a platinum susceptor. During the heating cycle, current vs. voltage curves were linear and the resistivity of the sample fell from 2×10^7 ohm-cm at 1035°C to 7×10^5 ohm-cm at 1270°C. After 2 hours at this temperature, the open-circuit emf was greater than +100 volts. The sample was left overnight without an applied voltage and in the morning the open-circuit emf was found to oscillate between 200 and -150 volts. High open-circuit emf's persisted throughout the day. After 48 hours the temperature was reduced, and below 1000°C there was no open-circuit emf. At 955°C a linear plot of current vs. voltage was obtained from 90 to 0 volts and it passed through the origin. The resistivity was calculated to be 7.3×10^8 ohm-cm. As the temperature was raised above 1000°C, an open-circuit voltage developed and increased rapidly to 340 volts at 1175°C. Further increases in temperature resulted in lowering of the open-circuit voltage. The voltage drop vs. temperature was almost linear, and at 1480°C it had dropped to 40 volts. At this temperature the platinum-rhodium susceptor failed when a slot melted the length of the tube. The magnesia sample lost 6.2 mg during the test.

c. Mercury Vapor Environment

A 1/2 inch thick sample of magnesia, tested for 100 hours in mercury vapor, had very little increase in its resistivity at maximum temperature throughout the test. Resistivity values are shown in Figure 43. Weight loss during testing was 4.6 mg (0.15 per cent). There was deposits on the tungsten rods above and below the sample. The cathode had a thin filmy deposit on its face, whereas the anode was still bright and shiny.

During the first 24 hours of testing, as the sample was heated, its current-voltage characteristics were linear, and up to 1230°C there was a very small rectified voltage by the sample of the same polarity as the impressed voltage. At 1260°C and above, the polarity of the rectified voltage was reversed. From 24 to 72 hours of test time, the I vs. E plots were still linear and the current from the rectified voltage had increased. After 72 hours of the test, the I-E curves were generally linear from 90 down to 60 or 40 volts and then were usually erratic.

Both ends of the sample were analyzed with an X-ray diffractometer, and only lines for magnesia were found. The relative intensities of the lines were not the same on both ends. The height of the peaks above background and the intensities reported by Swanson and Tatge are listed below:

	Height of Peak			
hkl	Negative End	Positive End	Untested	I*
111	62	40	18	10
200	>> 95	60	>> 95	100
220	>> 95	74	87	52
311	20	11	22	4
222	21	36	43	12
400	43	5	11	5

*H. E. Swanson, and E. Tatge, "Standard X-Ray Diffraction Powder Patterns," NBS Circular 539, Vol. 1.

Four series of resistance measurements using mercury vapor were made on one sample of magnesia. Between tests, the cooled sample was left undisturbed in the test apparatus. During the first test, the sample was heated without an applied voltage to 1310°C. Af this temperature, voltage was applied in 1-volt increments to 10 volts and in 5-volt steps from 10 to 90 volts. The slope of the straight-line curve from 0 to 20 volts was equivalent to a resistivity of 2.4×10^5 ohm-cm. Above 20 volts, the curve was complex, but on reducing the voltage back to 0 volts, a nearly linear curve was obtained which was equivalent in slope to a resistivity of 3.0 x 10^5 ohm-cm. The sample was then cooled with no applied voltage and with the circuit open. In the second test, the sample was again heated without a potential being applied. At 1300°C, a resistance test was made; following the test the 90-volt potential was reapplied and left on the sample after each resistance test as the sample cooled. During the third and fourth tests, the 90-volt applied potential was left on the sample during both heating and cooling cycles, except when the voltage was varied to obtain a resistance curve. All of the resistivity values calculated appear to lie on one line as shown in Figure 44, without any improvement in resistivity in the successive tests.

A sample of magnesia, 1/2 inch thick, was tested for 100 hours in cesium vapor with a hydrogen-argon carrier. Figure 45 shows the resistivity results of this test. During the first 24 hours, I vs. E plots were quite linear and intersected the origin. After this they were generally linear at the higher voltages and tended to be curved at the lower voltages, with a lessening rate of decrease in current with a decrease in voltage. Weight loss by the sample was only 0.5 mg (0.02 per cent).

X-ray diffraction analysis of the end surfaces after testing revealed only lines for magnesia. Again, the relative intensities of the lines differed from end to end. The height of the peaks above background and intensities reported by Swanson and Tatge are as follows:

	Height of Peak		
hkl	Negative End	Positive End	I^*
111	15	37	10
200	>>95	>>95	100
320	>>95	>>95	52
311	16	45	4
222	17	34	12
400		7	5
331		10	2
320		36	17

*H. E. Swanson and E. Tatge, loc. cit.

Four separate resistivity tests were made on a single sample of magnesia, 1/2 inch thick, in cesium vapor with a hydrogen-argon carrier. The sample and furnace were not disturbed between tests. Resistivity results obtained from heating and cooling curves are shown in Figure 46. The resistivity appears to increase with successive tests. I vs. E curves in the first tests were linear and intersected or came very close to the origin. In subsequent tests a rectified voltage tended to make the curves cross the ordinate at a slightly positive current with no applied voltage, and in the third and fourth tests the curves tended to depart from linearity below 20 volts when the rate of decrease in current increased with a reduction in voltage.

3. Beryllia

a. Nitrogen Environment

A 1/8 inch thick sample was tested twice in prepurified nitrogen containing 500 ppm hydrogen and was heated with a platinum susceptor. The sample was not disturbed between tests. Results of both tests are shown in Figure 47.

In both of the short-term tests of the 1/8 inch thick beryllia samples, the current vs. voltage curves wavered at times but, in general, were linear although they did not intersect the origin. The rapid decrease in resistivity above 1300°C (the slope would represent an activation energy of about 15 ev) brought the curve down to the curve obtained earlier for a 1/8 inch thick sample of beryllia. Below 1300°C the resistivities are almost two orders of magnitude larger than those previously observed and are very close to those obtained in cesium vapor with a carrier of nitrogen.

b. Hydrogen Environment

One sample of beryllia was tested for 100 hours twice in an argon-hydrogen atmosphere. During the first test, the sample was heated by a molybdenum susceptor, and in the second test, after resetting with the same electrodes, by a graphite susceptor. Results of these tests are shown in Figures 48 and 49.

Prior to the 100-hour tests, the sample was heated to 1270°C without an applied voltage. The largest open-circuit emf measured across the sample was 5.9 volts. As the sample was heated in the first 100-hour test, the current vs. voltage curves below 1100°C showed a slight change of current with changes in voltage at the higher test voltages and were nonlinear, whereas the curves were linear at the lower voltages. Between 1100° and 1200°C, the curves were linear at the higher voltages with very large, nonlinear changes in current with voltage changes in the lower voltage range. Above 1200°C, the curves had three linear portions between 90 and 0 volts, all with different slopes. After a few hours, the curves tended to straighten out. For the following three days, various types of current vs. voltage curves were obtained--some linear, and others with both linear and curved portions. On the fifth day, all currents were negative at 1300°C and remained so down to 1200°C.

After cooling, the sample was reset in the furnace with a graphite susceptor. During this second 100 hours, almost all of the current vs. voltage curves were linear from 90 to 0 volts.

The sample, which turned gray during the first test, was very dark after the second 100 hours. Weight loss in the first test was only 0.5 mg (0.02 per cent); however, in the second test, the sample lost an additional 3.7 mg (0.14 per cent).

Results of three short-term tests on one piece of beryllia 1/8 inch thick are shown in Figure 50. During testing, the positive end surface attained a high polish. When separated from the still polished anode, the two had to be slid apart like gage blocks. The positive end was still white after testing, whereas the negative end was gray. Weight loss was negligible, about 0.1 mg.

The resistivity curve of the 1/8 inch sample was appreciably higher than the curves for the 1/2 inch thick sample obtained in 100-hour tests. In both cases the curves agree very closely with those obtained in previous work,(2) in which similar samples were tested to about 1800°C.

c. Mercury Vapor Environment

Results of a 100-hour resistance test on a 1/2 inch thick sample of beryllia tested in mercury vapor with a carrier of hydrogen-argon are shown in Figure 51. During the first 8 hours of the test, currents through the sample were steady, and linear I vs. E plots were obtained from 90 to 20 volts. Below 20 volts the currents tended to fall at a more rapid rate as the voltage was reduced. As the test continued, the current due to the voltage rectified by the sample from the RF field increased.

Although plots of voltage and current after the first day exhibited scatter, resistivities calculated from the slopes of the plots fell in a narrow range. The slope of the resistivity curve is very steep in Figure 51. The apparently rapid change in resistivity with temperature may be caused by conduction effects due to changes in the sample during the test.

Four short-term tests were made on one piece of beryllia, 1/2 inch thick. During the first test, no voltage was applied to the sample as it was heated to 1300°C. Voltages developed across the sample possibly as a result of rectification of the RF field are shown in Figure 52, along with similar measurements made during the cooling cycle following a few resistance measurements made with applied voltages. Figure 52 also shows the open-circuit emf measured during the heating cycle of the second test.

Three resistance tests were made at about 1300°C in the first test over a period of 3 hours. During one resistance test, the voltage was raised in steps from 0 to 90 volts and current measured at each voltage step. Similarly, current measurements were made as the voltage was reduced to 0 volts. Results of the measurements are shown in the I vs.E curves in Figures 53 to 55. In the first two series of measurements interference to charge carriers appears to prevent the increase in current to a large extent above 15 to 20 volts.

In the third series of measurements shown in Figure 55, this effect is less pronounced and the curve appears to be straightening somewhat; however, after cooling and reheating, the curve obtained in Figure 56 is again very similar to that shown in Figure 54. Following the measurements for Figure 56, the potential across the sample was returned to 90 volts and the temperature and voltage were held constant. After an hour with voltage applied, the I vs. E curve was a bit ragged but fairly straight. As the temperature was reduced, the curves improved in linearity. A summary of the resistivity results obtained during the heating and cooling cycles is shown in Figure 57.

d. Cesium Vapor Environment

The resistivity of a 1/2 inch thick sample of beryllia increased about one order of magnitude at 1250°C during a 100-hour test in cesium vapor with a carrier of hydrogen-argon. Results of the test are shown in Figure 58. Weight change of the beryllia was negligible, a loss of 0.1 mg.

The current voltage characteristics were linear for most of the measurements, which were made between 90 and 0 volts. During the first day of testing reverse currents through the ammeter were obtained at several temperatures, generally only at the lower applied voltages. The resistivity curve obtained where the sample was cooled at the end of the test is slightly higher than that obtained from a similar sample tested in hydrogen-argon (Figure 48).

X-ray analysis with a diffractometer of both ends of this sample of beryllia revealed only reflections from beryllia; however, there were unusual intensifications of the reflections. In the following table the heights of the various reflection peaks above background are given for both end surfaces of the beryllia sample; also shown are relative intensities of the reflections in the same terms by Swanson and Tatge.

hkl	Height of Peak Negative End	Height of Peak Positive End	I*
101	>> 95	>> 95	100
102	46	77	22
110	95	58	29
103	52	> 95	24
200	15	7	4
112	27	58	16
201	24	19	5
004	0	2	> 1
202	6	5	3

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*H. E. Swanson and E. Tatge, loc. cit.

One sample of beryllia, 1/8 inch thick, was tested four times in cesium vapor with a hydrogen-argon carrier. The heating and cooling cycle curves for these four tests are shown in Figure 59. After the second test the positive current from the rectified voltage increased; also some scatter appeared in plots of I vs. E, probably as a result of slight variations in the rectified current. There was practically no change in the cooling cycle resistivity curves.

4. Boron Nitride

a. Nitrogen Environment

One piece of pyrolytic boron nitride, 1/8 inch thick, was tested three times in nitrogen. Results of the test are shown in Figure 60. Above 1300°C the current-voltage curves tended to be nonlinear. The sample lost 0.83 per cent weight, and the lateral surface was black after testing.

A sample of pyrolytic boron nitride was tested in nitrogen for 100 hours; however, resistivity data are shown in Figure 61 for only the first 72 hours. Linear current vs. voltage plots were obtained for the first few hours. By the fifth hour, the plots started to be curved with lower rate of change of current at the higher voltage than at the lower voltages. After 24 hours the current plots were mostly erratic and only two fairly good plots were obtained. From 72 hours on,the current, after decreasing as the voltage was reduced from 90 to about 40 volts, would increase to, usually, a maximum value at 10 to 20 volts. Below 10 volts the current rapidly decreased to zero. No attempt was made to calculate resistivities from these plots.

Resistivity results of a 100-hour test on a 9/64 inch thick sample of pyrolytic boron nitride in nitrogen-2 per cent hydrogen are shown in Figure 62. The sample was heated to 1260°C without an applied voltage. When voltages were applied, fairly linear plots of current vs. voltage were obtained between 0 and 180 volts both with increasing and decreasing voltage. Following this set of measurements, 90 volts was applied to the sample and left on between measurements. Up to 24 hours, current vs. voltage plots were linear, but then an increase in current occurred at 70 volts as the voltage was lowered. After the increase, the current decreased linearly with voltage decrease, but the slope was steeper than it was above 70 volts. By 48 hours the current increase at 70 volts had disappeared and at the higher voltages the current tended to remain constant with voltage changes. As the sample was cooled at the end of the test, the hump reappeared at 70 volts and moved towards lower voltages as cooling progressed.

b. Hydrogen Environment

A 5/32 inch thick sample of pyrolytic boron nitride was severely attacked by hydrogen during a 100-hour test. The sample, which lost 14.8 per cent of its weight presumably through the formation of boranes, appeared scalloped around the lateral surfaces as though some "cones" were preferentially attacked. Both edges were rounded, and end surfaces were attacked to a lesser extent. Thickness of the sample was reduced about 3 per cent. There was no weight change of either electrode. Resistivity results of the test are shown in Figure 63.

C. General Comments on Results

Measurements of electrical resistance were made during heating and cooling cycles and while the sample was at elevated temperatures for short and prolonged periods of time. Effective resistivities tend to improve with time as the sample is held at a high temperature with an applied voltage, perhaps as a result of the depletion of impurity charge carriers through migration and/or volatilization. In general, the various atmospheres seemed to have little effect on the resistance of the insulator materials tested. However, thermal history appears to affect the current vs. voltage curves.

In alumina, there appears to be some mechanism that blocks or traps charge carriers above a certain voltage. The voltage is dependent on thermal history in that the blocking occurs at lower voltages with increased time. A sample of high-purity alumina quenched in air from 1575°C showed suppression of current similar to that in an unquenched sample after almost 100 hours at 1300°C. Suppression in the Alucer alumina differed from that in the high-purity material. Initial application of test voltages to the Alucer alumina caused a suppression of current which persisted in later measurements. This effect may explain the apparently high resistivities shown by Alucer.

Alucer, when tested in hydrogen-argon or in mercury vapor with hydrogen-argon carrier, developed a transition in the range of 1100° to 1250°C. Generally, there was a hysteresis effect resulting in two transition temperatures. At the higher temperature, current through the ammeter would switch direction from all positive currents from 90 to 0 applied volts to all negative currents at all applied voltages from 90 to 0 volts. When the temperature was then reduced to the lower transition temperature, the currents would switch back so that positive currents were again obtained at all applied voltages. The switching points tended to become lower with increasing time. This switching effect was not noted in tests made in cesium vapor with either hydrogen-argon or nitrogen carriers nor in N_2-10% H_2.

Volatilization of alumina in hydrogen with the growth of whiskers in cooler parts of the furnace was again observed concomitantly with the formation of an aluminum nitride shell on the sample. A suggested explanation is that nitrogen, outgassed from the graphite susceptor or as an impurity in the argon mixed with the hydrogen, reacts with the hydrogen-reduced alumina on the surface of the sample.

The use of a graphite susceptor was shown to reduce the resistivity of alumina during repeated tests; whereas with a platinum or molybdenum susceptor the resistivity improved upon retesting, approaching, in the case of hydrogen atmosphere, the cooling cycle resistivity curve for sapphire.

X-ray diffraction analysis of the end surfaces of tested magnesia and beryllia revealed variations in the intensities of reflections from a normal pattern. Intensities from the positive end differed from those of the negative end. The differences may be due to orientation or distortion effects on the sample by the applied voltage at elevated temperatures or by impurities from the test atmosphere or electrodes. Beryllia samples would frequently have a very high polish on the positive end surface following resistance tests. The sample and the polished anode would tend to resist pulling apart but could be slid apart easily.

Magnesia, when tested for extended periods in nitrogen, appeared to react with the tungsten electrodes. In hydrogen, high-open circuit voltages developed which collapsed when the induction generator was turned off. The voltage-current curves were consistently more linear for magnesia than for the other materials that were tested.

Beryllia exhibited a suppression of current at the higher test voltages. When heated in hydrogen-argon with a graphite susceptor for 100 hours, a sample of beryllia had a weight loss of 0.14 per cent compared to a 0.02 per cent loss when similarly tested using a molybdenum susceptor.

Pyrolytic boron nitride appeared to be a very good insulator when tested for short periods of time during work on a previous contract.(2) In that work it was noted that the electrodes were affected by testing. In the present program, reactions between the insulator and tungsten electrodes during long-term tests were more severe. Long-term tests in hydrogen resulted in large weight losses believed to be caused by the formation of volatile boranes. The material does not appear suitable as an insulator in contact with tungsten because of the reactivity observed in resistance tests and in the interaction tests covered in Part III of this report.

III. INTERACTIONS BETWEEN REFRACTORY METALS AND CERAMICS

This portion of the program is concerned with the effects of elevated-temperature contact between ceramic insulator materials and refractory metals on the mechanical and other properties of the metal specimens. Most of the interaction studies were conducted at 1500°C; short-time exposures were usually for 5 hours, whereas the long time treatments ranged up to 100 hours. A DC voltage was applied to some of the metal-ceramic couples during heating, although the majority of exposures did not involve an applied voltage.

Of primary interest was the effect of elevated-temperature contact with the insulator materials under various atmospheres on the hardness, strength, ductile-to-brittle transition behavior, electrical resistivity, and other properties of the metals. Thus, from the standpoint of retention of the metal properties, the best combinations of metal, ceramic, and heating atmosphere could be ascertained.

A. Equipment and Procedures

1. Ceramic Materials

The ceramic materials used under this phase of the program were primarily in powder form, although some of the experiments were conducted using hot pressed or sintered rods and plate stock. Whenever possible, the same ceramic materials used under the preceding portion of the program were used for this phase of the work.

a. Alumina

Nearly all of the alumina used was in powder form, and two grades were used to investigate the effects of purity. Most of the interactions were conducted using a material supplied by AIAG Metals, Inc., grade RS-17 material which was in excess of 99.9 per cent purity. This powder was -325 mesh, and unless otherwise specified in the subsequent sections, was the alumina used. A few experiments were conducted using Agsco No. 36 alumina having a purity of approximately 99.5 per cent; the major impurities are silica, magnesia, and calcia. This material was screened to pass through 200 mesh.

Alumina slab, Wesgo AL 995, was also used for a few of the experiments. This material has a typical purity of 99.5 per cent, similar to that of the Agsco alumina powder.

b. Magnesia

The magnesia powder used for the interaction studies was Mallinckrodt AR grade; typical impurity contents were listed in section II-A-1-d of this report. It was found that the extreme fineness (< 1 micron) and low bulk density of this powder caused excessive shrinkage during the interaction studies. To increase the bulk density, pressed powder compacts were fired in air at 1700°C, then crushed to pass 200 mesh. These powders exhibited very little shrinkage during the subsequent 1500°C interaction treatments.

c. Boron Nitride

Pyrolytic boron nitride powders were prepared from the plate stock supplied by High Temperature Materials, Inc. After crushing and milling, these powders were screened through 200 mesh. This is the same material used under Part II of this program.

d. Beryllia

The beryllia used for these studies was grade F-1 supplied by the Brush Beryllium Company. Information regarding purity may be found under Section II-A-1-e of this report.

2. Refractory Metals and Alloys

a. Tungsten

Commercial high-purity tungsten rod measuring approximately 1/4 by 1/8 inch was supplied by Fansteel Metallurgical Corporation. This rod was cut into 2-inch lengths, and both large faces were surface ground to a depth of at least 0.008 inch to remove any possible surface contamination and to provide parallel faces for subsequent mechanical property tests. The material was in the warm-worked condition; recrystallization occurred during subsequent elevated temperature interaction treatments.

b. Tantalum

Tantalum sheet in two thickness ranges (0.030 and 0.060 inches) was supplied by Fansteel Metallurgical Corporation. This annealed sheet was sheared into 1/4 by 2 inch specimens; the edges were ground to provide a uniform specimen width.

c. 90Ta-10W Alloy

The tantalum-tungsten alloy sheet, 0.060 inch thick was also supplied by Fansteel Metallurgical Corporation. Test specimens measuring 1/4 by 2 inch were prepared by shearing and edge grinding.

d. Molybdenum

Stress-relieved molybdenum plate, 0.125 inch thick, was obtained from Fansteel Metallurgical Corporation. This stock was cut into 1/4 by 2 inch sections,and the edges were surface ground so that a uniform specimen width was obtained.

e. TZM Alloy

The molybdenum alloy TZM (Mo-0.5Ti-0.08Zr) was purchased as 0.125 inch stress-relieved plate from the Climax Molybdenum Company of Michigan. After sawing into 1/4 by 2 inch sections, the edges and large faces were surface ground.

3. Interaction Apparatus and Procedures

a. Furnaces

Two furnace types were used to conduct the elevated-temperature interactions between the metal and ceramic materials under investigation.. All of the heat treatments conducted under vacuum or under inert atmosphere utilized a National Research Corporation model 2914 furnace. The resistance-heated tantalum elements provide a hot zone approximately 4 inches in diameter by 6 inches long; multiple tantalum heat shields are used for insulation. Vacuum measurements at temperature showed pressures of 3 to 6 x 10^{-6} torr during these investigations.

Tube-type furnaces were used for heat treatments in hydrogen or nitrogen atmospheres. The furnace used for hydrogen consisted of a high-purity alumina muffle with a spiral wound molybdenum wire heating element. Both the tubular muffle and winding were encased in a gas-tight box which was filled with hydrogen. Nitrogen furnace runs were conducted in a gas-tight zirconia tube in a Globar-type furnace capable of attaining 1500°C.

The tank gases used in these experiments were purified by passing them over hot titanium sponge and through a liquid nitrogen trap. In addition, the hydrogen was first passed through a palladium-coated alumina catalyst to convert any oxygen to water vapor where it could be removed in an activated alumina drying tower.

b. Test Setups for Interaction Studies

Two basic types of test setup were used, depending on whether or not a voltage was applied across the metal-ceramic couple. In the case of interactions in the presence of a DC voltage, the ceramic material was in slab or plate form. A typical test setup is illustrated in Figure 64.

Each high-temperature furnace run contained five or six refractory metal bar specimens for modulus of rupture determinations. These bars were loaded as illustrated in Figure 64 for tungsten-aluminum oxide couples. It may be seen that the two bottom transverse-rupture specimens were not in contact with any ceramic material. The next higher pair of specimens were in electrical contact with the insulator material on both top and bottom surfaces; the desired high resistance in the case of alumina was obtained by the use of flat 3/16-inch thick slabs which were approximately 1/2 inch long and were centrally located with respect to the metal specimen length. A voltage source (90 VDC) was applied to a pair of tungsten spacers through tungsten wire which was spot-welded to the spacers; current measurements were taken throughout the heating and cooling cycle. The upper tungsten specimens were in contact with the ceramic material on one face, but no voltage was applied. Heating of these assemblies was performed under hydrogen gas which was passed through a palladium catalyst, an activated alumina dryer, and a phosphorus pentoxide tower. No sagging of the bars was observed during the exposure, and the appearance of the specimens indicated that a good contact was obtained between metal and refractory.

Most of the metal-ceramic interaction studies were conducted without an applied voltage. For these studies, the ceramic material was in the form of -200 or -325 mesh powders. The following procedure was used to prepare a test setup for elevated-temperature exposure:

1. A layer of powdered ceramic material approximately 1/8 inch thick was placed in the bottom of a tantalum box (molybdenum was used in the case of hydrogen).

2. Metal test specimens, usually 1/8 x 1/4 x 2 inch, were placed with one of the large faces resting on top of the layer of powdered ceramic material.

3. Additional ceramic powder was poured in the box until the powder layer was at least 1/8 inch above the top surfaces of the metal specimens.

4. Additional metal samples (control specimens) were wrapped in tantalum or molybdenum foil and placed on top of the powdered ceramic.

5. A loose-fitting cover was placed over the tantalum box which contained the metal test specimens and the ceramic material.

In some cases, more than one layer of metal specimens was contained within a box; the layers of metal samples were separated by a thickness of at least 1/8 inch of the powdered ceramic material. The ceramic powders were replaced with fresh material after exposures in excess of 20 hours.

c. Elevated-Temperature Furnace Procedures

The metal-ceramic setups, either in boxes with the powdered ceramic or in stacks with ceramic slabs and appropriate electrical leads, were placed in the furnace at room temperature. The furnace tube or heating chamber was then purged for a sufficient length of time to exclude air from the chamber and from the specimen setups; 1 to 2 hours was sufficient in most cases. After purging, furnace heat was applied and the contents brought to temperature (usually 1500°C) at a uniform rate in 1 to 1 1/2 hours. Furnace runs were generally 5 to 7 hours at temperature, after which the loads were cooled to room temperature in approximately 2 hours. For the long-time runs, this procedure was repeated to accumulate the desired number of hours at temperature. Powdered ceramic material was replaced after a total of 20 hours of elevated temperature exposure.

4. Evaluation Methods

a. Hardness

Vickers pyramid hardness indentations (VPN) were taken on the surfaces of the metal specimens. In many cases, the interaction with the ceramic material required that the surfaces be polished lightly with 600 grit silicon carbide paper. The load used was usually 1 kg, although 2.5 kg was used when surface layers were relatively thick.

The specimens were then sectioned and mounted in a castable hard polymer so that the transverse sections could be polished and examined metallographically. Vickers hardness measurements were taken on these polished sections so that core hardness values (VPN 2.5 to 5 kg) could be measured.

b. Strength Measurements

Transverse-rupture tests were conducted at temperatures up to 1100°C on 1/4 by 2 inch specimens which had thicknesses ranging from 0.06 to 0.125 inch. A three-point loading device having a 1.25 inch support span was used, and a crosshead speed of 0.05 in/min was employed. In the case of specimens which had been in contact with ceramics under an applied voltage, the contact surface of interest (anode or cathode) was in tension during loading. The modulus of rupture was calculated from the standard formula for rectangular beam specimens as follows:

$$\text{Modulus of rupture (psi)} = \frac{3Pl}{2\,wt^2}$$

where P = load, lb

l = support span, inch

w = specimen width, inch

t = specimen thickness, inch

Ductility was estimated by the crosshead travel prior to fracture. In the case of the more ductile specimens, no fracture occurred after a crosshead movement of 0.6 inch, the maximum distance possible with this apparatus. For a specimen 1/8 inch thick, this bend approximates a bend radius 1 1/2 times the specimen thickness.

c. Electrical Resistivity

The rectangular bar specimens 2 inches long were evaluated for electrical resistivity at room temperature. End portions of these samples were polished to remove any surface films in order to insure good electrical contact. A standard Kelvin bridge apparatus was used.

B. Experimental Results

Property data were obtained for five refractory metals or alloys which had been heated for varying lengths of time in contact with four different ceramic materials under hydrogen, nitrogen, inert gas (helium or argon), and vacuum. In some cases, a DC voltage was applied to the metal-ceramic couples. Table I indicates the range of combinations of metals, ceramics, and atmospheres studied under this phase of the program. The following sections present the experimental results.

1. Tungsten

a. Alumina

Tungsten-alumina couples were heated at temperatures up to 1600°C under hydrogen with an applied DC voltage and at 1500°C under hydrogen, nitrogen, helium, and vacuum without an applied voltage.

TABLE I

SCOPE OF INVESTIGATIONS OF METAL-CERAMIC COMBINATIONS HEATED UNDER VARIOUS ATMOSPHERES

Metal	Atmosphere Used for Ceramic Combination			
	Al_2O_3	MgO	BN	BeO
Tungsten	Hydrogen, p. 42*	Hydrogen, p. 46	Hydrogen, p. 48	Inert, p. 51
	Nitrogen, p. 44	Nitrogen, p. 47	Nitrogen, p. 49	
	Inert, p. 44	Inert, p. 47	Inert, p. 49	
	Vacuum, p. 45	Vacuum, p. 47	Vacuum, p. 50	
Tantalum	Nitrogen, p. 52	Nitrogen, p. 53	Nitrogen, p. 55	
	Vacuum, p. 52	Vacuum, p. 53	Vacuum, p. 55	
Ta-10W	Nitrogen, p. 56	Nitrogen, p. 58	Nitrogen, p. 60	Inert, p. 61
	Inert, p. 57	Inert, p. 58	Inert, p. 60	
	Vacuum, p. 57	Vacuum, p. 59	Vacuum, p. 60	
Molybdenum	Hydrogen, p. 62	Hydrogen, p. 63	Hydrogen, p. 64	Inert, p. 64
	Nitrogen, p. 62	Nitrogen, p. 63	Nitrogen, p. 64	
Molybdenum Alloy TZM	Hydrogen, p. 65	Hydrogen, p. 66	Hydrogen, p. 68	Inert, p. 70
	Nitrogen, p. 65	Nitrogen, p. 67	Nitrogen, p. 68	
	Vacuum, p. 65	Vacuum, p. 67	Vacuum, p. 69	

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* Page numbers referring to test results are supplied for quick reference.

(1) W-Al_2O_3 Under Hydrogen

A cursory study of the effects of an applied DC voltage on tungsten heated in contact with alumina was conducted under hydrogen at temperatures ranging from 1180° to 1600°C. Hardness and modulus of rupture data are presented in Table II.

These data show that tungsten, when annealed in contact with high-purity Al_2O_3 under hydrogen at temperatures below the recrystallization range, is little affected by an applied DC voltage or by contact with the ceramic without an applied voltage. The data for the first three furnace runs at 1180° to 1280°C show a range of about 150, 000 psi to slightly above 200, 000 psi for the modulus of rupture values. This spread may be expected for tungsten bar stock which has been annealed at temperatures very near that at which recrystallization occurs. The strength variation within a single furnace run ranged from about 14, 000 to 43, 000 psi in the unrecrystallized material. No trends were observed in the strength properties when the anode or cathode contact surfaces were stressed in tension. Hardness data for the 1180° to 1280°C runs showed only minor variations; a general lowering of hardness was noted with increasing time at 1180°C and also when the temperature was raised to 1280°C.

Considerable differences in mechanical properties were observed for the tungsten specimens annealed in contact with alumina at 1500° and 1600°C. These annealing temperatures produced complete recrystallization of the wrought bar stock, and in all cases the strength values for the specimens in contact with alumina under an applied voltage were lower than the values obtained for specimens which were not in contact with the insulator material. For the three high-temperature exposures with Al_2O_3, the lowest strength values were found when the cathode surface was loaded in tension. Modulus of rupture values as low as 62, 000 psi were measured; this is equivalent to an ultimate tensile strength of about 35, 000 psi.

TABLE II

ROOM-TEMPERATURE MECHANICAL PROPERTY DATA FOR TUNGSTEN HEATED IN CONTACT WITH CERAMICS UNDER HYDROGEN

			Modulus of Rupture, psi				Surface Hardness (2.5 kg) VPN		
			No Applied Voltage		90 VDC Applied Voltage				
Ceramic Material	Temp., °C	Time, hr	No Ceramic Contact	Ceramic Contact Side in Tension	Anode Side in Tension	Cathode Side in Tension	No Contact	Anode Contact	Cathode Contact
Al_2O_3 (a)	1180	4.5	198,000	-	166,000	147,000	525	525	530
Al_2O_3 (b)	1180	6	190,000	184,000	209,000	-	520	520	520
Al_2O_3 (b)	1280	3	153,000	169,000	156,000	172,000	490	495	490
Al_2O_3 (a)	1500	3	129,000	154,000	128,000	62,000	415	420	415
Al_2O_3 (c)	1500	3	143,000	147,000	103,000	96,000	415	410	420
Al_2O_3 (a)	1600	4	159,000	181,000	145,000	129,000	420	415	420

(a) Wesgo Grade AL-995

(b) AIAG Grade RS-17

(c) Agsco, Grade No. 36

It was subsequently found that tungsten specimens, from the same lot which had been embedded in alumina powder and recrystallized at 1500°C under hydrogen, exhibited a range of rupture strength values from 98,300 to 134,500 psi. These results indicate the large variations in strength found in tungsten specimens recrystallized under the same conditions. Thus, most of the variation in data found in Table II appears to be within the range of sample-to-sample variation for this particular lot of tungsten. Metallographic observation did not reveal the presence of surface layers or grain boundary phases in any of the specimens.

(2) W-Al_2O_3 under Nitrogen

Specimens of tungsten heated for 10 hours at 1500°C in contact with alumina under a nitrogen atmosphere had surface hardness levels of VPN 425 to 435. This same variation in hardness was found in the control specimens which had been wrapped in molybdenum foil during the same furnace run. No metallographic evidence of surface reactions was found, but modulus of rupture values were somewhat low (70,000-95,000 psi). It may be concluded that no significant property deteriorations occurred during the 10-hour, 1500°C exposure.

(3) W-Al_2O_3 under Helium

Tungsten specimens were heated for 21 hours at 1500°C in contact with the same high purity alumina (AIAG Grade RS-17); a purified helium atmosphere was used. Surface and core hardness values were in the VPN 435 to 445 range for the control specimens as well as the specimens in contact with the alumina. Electrical resistivity of the samples remained constant at approximately 5.9 microhm-cm. While these values are slightly higher than those reported for the specimens heated under vacuum, little difference in properties could be found between surface and core of the specimens. Likewise, the properties of the control specimens were nearly identical to the properties of the samples which were in contact with the alumina. There was no metallographic evidence of structural changes after 21-hour exposure under helium.

(4) W-Al_2O_3 under Vacuum

Tungsten specimens were heated in contact with the high purity AIAG RS-17 alumina powder for 98 hours at 1500°C. Property data for these specimens, together with data for the control specimens which were included in the same furnace but were not in contact with the ceramic material, are included in Table III. All hardness values were in the VPN 420-440 range, indicating that the 98-hour treatment had very little effect upon this property. Likewise, there was very little change in transverse-rupture strength and in electrical conductivity after this elevated temperature exposure. Ductile bend behavior was obtained at 400°C indicating that the 98-hour treatment had very little effect on ductile-to-brittle transition behavior. Metallographic examination did not reveal the presence of surface layers or any other major structural changes after 98 hours in contact with alumina.

TABLE III

ROOM-TEMPERATURE PROPERTIES OF TUNGSTEN AFTER 98 HOURS AT 1500°C IN VACUUM WITH Al_2O_3

Property	Before Heat Treatment	After 98 hours in vacuum	
		In Contact with Al_2O_3	No Ceramic Contact
Surface hardness, VPN 2.5 kg	425	420	440
Core hardness, VPN 2.5 kg	425	430	430
Modulus of rupture, psi	-	135, 300	126, 300
Electrical resistivity, microhm-cm	5.6	5.7	5.5

b. Magnesia

Tungsten was heated in contact with MgO under hydrogen at 1500° and 1600°C with an applied voltage, and under hydrogen, nitrogen, inert atmosphere, and vacuum at 1500°C without an applied voltage.

(1) W-MgO under Hydrogen

Tungsten specimens were heated in contact with magnesia in a hydrogen atmosphere for 3 hours at 1500°C and 4 hours at 1600°C; a 90 VDC was applied to some of the tungsten-magnesia couples. Room-temperature property data (Table IV) show that the hydrogen exposures had little effect on the hardness and strength properties except for one low-strength specimen which possibly contained a surface flaw. The variation in strength values for the remaining samples was very slight, and within the range expected for fully recrystallized tungsten. No evidence of surface reaction or other structural changes was observed during these relatively short exposures.

TABLE IV

ROOM-TEMPERATURE MECHANICAL PROPERTY DATA FOR TUNGSTEN HEATED IN CONTACT WITH MAGNESIA UNDER HYDROGEN

Annealing		Specimen Surface Tested in Tension	Modulus of Rupture, psi	Hardness, VPN (2.5 kg)
Temp., °C	Time, hr			
1500	3	No contact with MgO	144, 300	420
		W-MgO, no voltage	154, 500	417
		W-MgO, anode	149, 600	423
		W-MgO, cathode	139, 400	420
1600	4	No contact with MgO	152, 700	423
		W-MgO, no voltage	156, 100	430
		W-MgO, anode	106, 200	428
		W-MgO, cathode	144, 500	430

(2) W-MgO under Nitrogen

Tungsten specimens embedded in magnesia powder were heated under nitrogen for 10 hours at 1500°C. The surface and core hardness measurements were within the VPN 425 to 435 range; the same hardness variations were found in the control specimens which were not in contact with magnesia. Metallographic examination did not reveal the presence of surface reactions or other structural changes.

(3) W-MgO under Helium

Tungsten specimens were heated in contact with magnesia for 21 hours at 1500°C under a highly purified helium atmosphere. Surface hardness values were VPN 437, while a hardness of VPN 450 was measured for the core. Virtually no change in electrical resistivity was measured. Similar results were obtained on the control specimens which were not in contact with the magnesia. No reason is apparent for the slight hardness increase of the core. This slight increase did not appear to alter the room-temperature transverse-rupture strength which was 130, 000 psi.

(4) W-MgO under Vacuum

Interaction studies of tungsten-magnesia couples were carried out for 98 hours at 1500°C under vacuum. The results of room-temperature hardness and electrical resistivity measurements are presented in Table V. A slight reduction in surface hardness was measured, although the bend strength was similar to that of the control specimens. A very slight increase in electrical resistivity was noted after the 98-hour exposure. The ductile-to-brittle transition temperature was relatively unchanged, as ductile bend behavior was noted at 400°C for the control specimen and also the sample heated in contact with magnesia.

Metallographic examination of the 98-hour specimens disclosed the presence of a surface layer (0. 025 inch thick) of relatively fine but recrystallized tungsten grains. The grains in the underlying core were much coarser, and approximately the same size as those found throughout the control specimen which was not in contact with magnesia. Apparently the presence of magnesia prevented growth of the tungsten grains near the surface.

TABLE V

ROOM-TEMPERATURE PROPERTIES OF TUNGSTEN AFTER 98 HOURS AT 1500°C IN VACUUM WITH MgO

Property	Before Heat Treatment	After 98 hours in Vacuum: In Contact with MgO	After 98 hours in Vacuum: No Ceramic Contact
Surface hardness, VPN 2.5 kg	425	420	440
Core hardness, VPN 2.5 kg	425	435	430
Modulus of rupture, psi	-	126,000	126,300
Electrical restivity, microhm-cm	6.2	7.8	6.2

c. Boron Nitride

Tungsten-boron nitride interaction studies were carried out with an applied DC voltage under hydrogen and argon, and without an applied voltage under hydrogen, nitrogen, argon, helium, and vacuum.

(1) W BN under Hydrogen

Tungsten specimens were heated in contact with boron nitride under a hydrogen atmosphere for 3 hours at 1500°C and 4 hours at 1600°C; these furnace runs included couples having a 90 VDC applied.

After 3 hours at 1500°C, the following property measurements were made at room temperature:

Sample	Surface Hardness, VPN (2.5 kg)	Transverse-Rupture Strength, psi
No contact with BN	420	125,000
W-BN, anode in tension	535	60,000
W-BN, cathode in tension	535	66,000

Contact with boron nitride caused higher surface hardness and reduced strength regardless of the polarity of the current. After 4 hours at 1600°C, surface hardness values were increased to VPN 630, and the rupture strength dropped to 51,000 psi for the anode surface and 61,000 psi for the cathode surface in tension. These specimens contained a very thin (< 0.001 in.) layer of a hard compound, probably a boride. Analysis of tungsten wires which had been heated in contact with boron nitride in electrothermal engines showed the presence of tungsten boride.(3)

(2) W-BN under Nitrogen

Virtually no increase in surface hardness of tungsten was measured after 20-hour exposure to boron nitride at 1500°C under an atmosphere of nitrogen. Under the other test atmospheres studied (hydrogen, argon, or vacuum) a hard compound layer was formed in relatively short heating times. Metallographic studies of the tungsten samples heated in contact with boron nitride under nitrogen did not show the presence of the hard layer except in a few areas of one specimen. This particular sample ha been heated in the molybdenum resistor furnace in which the nitrogen atmosphere was virtually static. The other specimens, which did not exhibit boride areas, were heated in the tube furnace under an atmosphere of flowing nitrogen. These results suggested that the boron nitride is relatively stable as long as a sufficient supply of nitrogen is available.

To further clarify this behavior, an additional 5-hour, 1500°C exposure was made wherein the tungsten samples were tightly packed in boron nitride except for the top surfaces which were covered with loose boron nitride powder. It was found that no compound had formed on the top surfaces which had free access to nitrogen, whereas the bottom surfaces had numerous areas of the hard surface layer.

(3) W-BN under Argon

The effects of short-time elevated-temperature contact with boron nitride on the ductile-to-brittle transition behavior of tungsten were studied. Specimens were heated for 2 hours at 1600°C under argon to produce an extremely thin (<0.001 inch) surface layer of the hard compound; the surface hardness increased from VPN 425 to 525. Bend tests were conducted at temperatures up to 540°C with the following results:

Specimen	Temp., °C	Rupture, psi	Remarks
No contact with BN	315	104,000	Ductile bend
Heated in contact with BN	315	42,000	Brittle
Heated in contact with BN	425	49,500	Brittle
Heated in contact with BN	540	90,000	Ductile bend

These results show that the bend transition temperature was increased from below 315°C to above 425°C by this 2-hour treatment in contact with boron nitride.

(4) W-BN under Helium

Tungsten specimens were heated for 21 hours at 1500°C in contact with boron nitride powder. A slight increase in electrical restivity (from 6.0 to 6.3 microhm-cm) was noted, and the core hardness rose from VPN 430 to 483. Surface hardness values were VPN 1185 after 14 hours and VPN 1450 after 21 hours. The hard boride layer was approximately 0.002 inch thick after the latter exposure. These results are similar to those obtained under vacuum.

(5) W-BN under Vacuum

Tungsten-boron nitride interaction studies were conducted under a high vacuum for 98 hours at 1500°C. The results of room temperature hardness, strength, and electrical resistivity measurements are summarized in Table VI. These data clearly indicate the extent to which tungsten is hardened and weakened by prolonged contact with boron nitride. The modulus of rupture value of 31,000 psi is equivalent to a tensile strength of about 17,000 psi. An example of the severe embrittlement was shown when a 1/8 by 1/4 by 2 inch sample fractured when accidently dropped onto a tile floor. The surface hardness increased rapidly with time at 1500°C; some areas were VPN 1700 after 21 hours. More detailed curves showing the variations in hardness with time are shown in Section III-C of this report where the relative stability of the various metal-ceramic-atmosphere combinations are compared.

TABLE VI

ROOM-TEMPERATURE PROPERTIES OF TUNGSTEN AFTER 98 HOURS AT 1500°C IN VACUUM WITH BN

Property	Before Heat Treatment	After 98 hours in Vacuum	
		In Contact with BN	No Ceramic Contact
Surface hardness, VPN, 2.5 kg	425	1800+	440
Core hardness, VPN 2.5 kg	425	430	430
Modulus of rupture, psi	-	31,000	126,300
Electrical resisticity microhm-cm	6.1	7.1	6.1

Metallographic observations revealed the presence of a hard compound layer approximately 0.005 inch thick. This layer was remarkably tenacious, and the structure (Figure 65) consisted of columnar grains of the hard compound which were well anchored in the tungsten. Microhardness measurements in the tungsten areas between these columnar grains showed the matrix to be relatively soft (near VPN 500).

d. Beryllia

A single exposure, 10 hours at 1500°C, waa made for tungsten in contact with beryllia under argon. Virtually no change in hardness was measured, and no evidence of an interaction was observed. The modulus of rupture of the tungsten after this exposure was 121,000 psi, a value similar to that of the control specimen which was not in contact with beryllia.

2. Tantalum

a. Alumina

Tantalum was heated in contact with alumina under nitrogen and also under vacuum for up to 98 hours at 1500°C. No exposures were made under hydrogen because of the susceptibility of tantalum to hydride formation.

(1) Ta-Al_2O_3 under Nitrogen

Tantalum was severely embrittled when heated in contact with alumina under a nitrogen atmosphere for 5 hours at 1500°C. The surface hardness increased from VPN 120 to the range of VPN 800 to 1300. Much of this hardening was due to the effects of nitrogen, as the control samples not in contact with alumina had similar hardness values. Tantalum is known to absorb appreciable quantities of nitrogen at 1500°C, and the hardening effect is principally that of solid solution. Some nitride compound formations were noted on specimens which were slowly cooled from 1500°C.

(2) Ta-Al_2O_3 under Vacuum

Tantalum specimens were heated in contact with the high purity RS-17 alumina powder for 98 hours at 1500°C under a high vacuum. A steady rise in surface and core hardness was noted during the course of this exposure; after 100 hours the specimens had a uniform hardness of VPN 689 throughout the samples. The electrical resistivity rose uniformly from a value of 16.1 microhm-cm to 31.1 microhm-cm after 98 hours. A considerable coarsening of the tantalum grains was observed after this exposure.

Bend tests on the 98-hour specimens were conducted at temperatures up to 800°C. At room temperature and at 400°C, the specimens were weak and brittle. A test conducted at 600°C resulted in a partially ductile bend, and the specimen tested at 800°C was fully ductile. Thus the bend transition temperature was increased to approximately 600°C. The mechanical and other properties of tantalum after 98 hours of exposure to Al_2O_3 under vacuum are summarized in Table VII.

TABLE VII

ROOM-TEMPERATURE PROPERTIES OF TANTALUM AFTER 98 HOURS AT 1500°C IN VACUUM WITH Al_2O_3

Property	Before Heat Treatment	After 98 hours in Vacuum	
		In Contact with Al_2O_3	No Ceramic Contact
Surface hardness, VPN 2.5 kg	120	689	150
Core hardness, VPN 2.5 kg	120	689	150
Bend transition temperature, °C	subzero	600	subzero
Electrical resistivity, microhm-cm	13.1	31.1	14.1

b. Magnesia

Tantalum-magnesia interaction studies were conducted under nitrogen and under vacuum for up to 98 hours at 1500°C.

(1) Ta-MgO under Nitrogen

Four furnace runs, each for 5 hours at 1500°C, were made with tantalum embedded in magnesia powder. These runs differed primarily with respect to nitrogen flow rate and cooling rate from 1500°C. It was found that the tantalum specimens in all cases had very high surface hardnesses--VPN 1200 to 1600. Since the control specimens exhibited hardnesses in the VPN 900 to 1300 range, it can be concluded that most of the hardening was due to nitrogen rather than to contact with magnesia.

(2) Ta-MgO under Vacuum

Tantalum specimens were heated in contact with magnesia for 98 hours at 1500°C under vacuum. The surface hardness rose from VPN 122 to 376 in 7 hours. During the remaining 91 hours, the surface and core hardness increased only slightly to a value of VPN 440. Electrical resistivity increased rapidly to a peak value of 38.1 microhm-cm in 21 hours, then dropped to 29.6 microhm-cm after 49 hours. No value for resistivity was obtained after 98 hours because of excessive specimen warpage. Metallographic examination showed that a hard phase, probably an oxide, had penetrated completely throughout the specimens after 49 hours. This phase existed as globules in the grain boundaries and also as an oriented precipitate within the grains, as shown in Figure 66.

Transverse-rupture tests were conducted on the 98-hour exposure specimens at temperatures up to 1100°C. Brittle fractures were obtained up to 800°C, while some ductility was evidenced at 1100°C. Thus the bend transition temperature of these specimens was between 800° and 1100°C, and probably much closer to the latter temperature. These data, together with other properties of the 98-hour exposure specimens are summarized in Table VIII.

TABLE VIII

ROOM-TEMPERATURE PROPERTIES OF TANTALUM AFTER 98 HOURS AT 1500°C IN VACUUM WITH MgO

Property	Before Heat Treatment	After 98 hours in Vacuum: In Contact with MgO	After 98 hours in Vacuum: No Ceramic Contact
Surface hardness, VPN 2.5 kg	120	440	150
Core hardness, VPN 2.5 kg	120	440	150
Bend transition temperature, °C	subzero	~1000	subzero
Electrical resistivity, microhm-cm	13.1	38.1(a)	14.1

(a) Peak value after 21 hours

c. Boron Nitride

Tantalum-boron nitride couples were heated under nitrogen for 5 hours at 1500°C, and also under vacuum for 98 hours at 1500°C.

(1) Ta-BN under Nitrogen

Four 5-hour exposures using varying nitrogen flow rates were made at 1500°C for tantalum specimens embedded in boron nitride. Three of the heat treatments were carried out using comparatively high nitrogen flow rates. The tantalum specimens had surface hardnesses of VPN 740-890 whether or not they were in contact with boron nitride. Thus the hardening effect is that of nitrogen solid solution, and the abundant supply of nitrogen apparently prevented decomposition of boron nitride at the tantalum surface. The fourth 5-hour exposure was done under a static nitrogen atmosphere, and somewhat higher surface hardness values (VPN 1400) were obtained. Metallographic examination showed the presence of small areas of the hard phase, presumably a tantalum boride, on the metal surfaces. These samples also showed the same acicular precipitate found in the control specimens, believed to be tantalum nitride.

(2) Ta-BN under Vacuum

Tantalum-boron nitride interaction studies were carried out for 98 hours at 1500°C under vacuum. Surface hardness values increased rapidly: VPN 974 in 7 hours; VPN 1650 in 21 hours; and VPN 1850+ in 49 hours. During the first 7-hour exposure, the core hardness increased very rapidly to a value of VPN 660; however, the core hardness was VPN 782 after 98 hours. Electrical resistivity also increased rapidly during the first 7 hours to 27.8 microhm-cm. There was very little further increase in resistivity during the remainder of the 98-hour exposure.

Metallographic observation disclosed a single-phase core structure with a surface layer of columnar grains of a very hard phase. This layer was about 0.005 inch thick, and was similar to that shown in Figure 65.

Bend tests were conducted at temperatures up to 1100°C. All of the specimens fractured in a brittle manner at very low load levels. These and other property data for the 98-hour exposure are summarized in Table IX.

TABLE IX

ROOM-TEMPERATURE PROPERTIES OF TANTALUM AFTER 98 HOURS AT 1500°C IN VACUUM WITH BN

Property	Before Heat Treatment	After 98 hours in Vacuum	
		In Contact with BN	No Ceramic Contact
Surface hardness, VPN 2.5kg	120	1850+	150
Core hardness, VPN 2.5kg	120	782	150
Bend transition temperature, °C	subzero	1100+	subzero
Electrical resistivity, microhm-cm	13.1	29.3	14.1

3. 90Ta-10W Alloy

The commercial tantalum alloy, 90Ta-10W, is characterized by good fabricability with a much higher recrystallization temperature and elevated temperature strength than pure tantalum. This alloy was exposed to the ceramic materials under all atmospheres except hydrogen; the latter was not used because of hydride formation.

a. Alumina

The 90Ta-10W alloy was heated in contact with alumina under nitrogen, helium, and vacuum for up to 98 hours at 1500°C.

(1) (90Ta-10W)-Al_2O_3 under Nitrogen

Specimens of the 90Ta-10W alloy were heated in contact with alumina under a nitrogen atmosphere at 1500°C. Four 5-hour exposures using varying nitrogen flow rates were made. In all cases very high surface hardnesses (VPN 1500-1700) were measured, not only for the samples heated in contact with alumina but also for the control specimens which had been wrapped in molybdenum foil. These hardnesses are higher than values measured for unalloyed tantalum which had a similar exposure. The hardening was due primarily to nitrogen and not to contact with alumina.

(2) (90Ta-10W)-Al_2O_3 under Helium

Interaction studies of 90Ta-10W with alumina were conducted under helium for 21 hours at 1500°C. Surface and core hardnesses increased to VPN 394 and 353, respectively, after 21 hours. This rate of hardening was slightly higher than that measured when the exposure was made under vacuum. The electrical resistivity rose from 17.3 to 20.0 microhm-cm, also a slightly higher rate of increase than was measured after exposure in vacuum. There was no evidence of surface reaction or other phases in the microstructures.

(3) (90Ta-10W)-Al_2O_3 under Vacuum

Interaction studies of the 90Ta-10W alloy with alumina were carried out for 98 hours under vacuum at 1500°C. Hardness data showed that both the surface and core increased gradually in hardness to values near VPN 620 after 98 hours; hardness levels of the control specimens increased from VPN 220 to 250 during this exposure. The electrical resistivity of the specimens heated in contact with alumina also increased gradually during the 98-hour period to a value of 27.2 microhm-cm. Metallographic examination did not reveal the presence of surface layers or other phases in the alloy matrix. The ductile-to-brittle temperature, as determined by bend tests, was above 1100°C. Pertinent data are summarized in Table X.

b. Magnesia

Exposure of 90Ta-10W embedded in magnesia were made under nitrogen, helium, and vacuum at 1500°C.

TABLE X

ROOM-TEMPERATURE PROPERTIES OF 90Ta-10W AFTER 98 HOURS AT 1500°C IN VACUUM WITH Al_2O_3

Property	Before Heat Treatment	After 98 hours in Vacuum: In Contact with Al_2O_3	After 98 hours in Vacuum: No Ceramic Contact
Surface hardness, VPN 2.5kg	230	623	250
Core hardness, VPN 2.5 kg	230	612	250
Bend transition temperature, °C	<20	1100+	<20
Electrical resistivity, microhm-cm	17.5	27.2	18.1

(1) (90Ta-10W)-MgO under Nitrogen

All of the 90Ta-10W alloy specimens heated under a nitrogen atmosphere for 5 hours at 1500°C exhibited exceptionally high surface hardness. Values of VPN 1500 to 1700 were measured for the specimens embedded in alumina and also for the control samples wrapped in molybdenum foil. Thus the primary hardening mechanism is that of nitrogen solid solution. Much higher hardnesses were measured for the 90Ta-10W alloy than for unalloyed tantalum exposed to the same atmosphere.

(2) (90Ta-10W)-MgO under Helium

Interactions between the 90Ta-10W alloy and magnesia under helium were similar to those observed under vacuum. A rapid rise in surface and core hardness occurred during the first 7 hours, with very little additional increase during the remaining 14 hours of the helium exposure. The microstructures after 21 hours contained a grain boundary phase near the surface; this structure was similar to that shown in Figure 67.

(3) (90Ta-10W)-MgO under Vacuum

Specimens of 90Ta-10W were embedded in magnesia and heated under vacuum for 98 hours at 1500°C. Rapid hardness increases of both surface and core to about VPN 500 were observed during the first 7 hours of exposure; very little additional increase in hardness occurred during the subsequent 91 hours. The electrical resistivity reached a peak value of 59.2 microhm-cm after 21 hours, then dropped to 34.3 microhm-cm after 49 hours. It was not possible to obtain a resistivity measurement after the 98-hour exposure because of excessive warpage of the sample.

These specimens had unique microstructures in that a very hard phase, probably an oxide, occupied the grain boundaries as a rather uniform, thick massive deposit. This grain boundary phase was evident near the specimen surfaces after the first 7 hours at 1500°C, and the layer containing this phase grew thicker with increasing time. Figure 67 is a photomicrograph showing this grain boundary compound after the 98-hour exposure in contact with magnesia at 1500°C.

Specimens having the 98-hour exposure were subjected to bend tests at temperatures up to 1100°C. In all cases, the material exhibited brittle fractures at very low stress levels. These data, together with other properties, are summarized in Table XI.

TABLE XI

ROOM-TEMPERATURE PROPERTIES OF 90Ta-10W AFTER 98 HOURS AT 1500°C IN VACUUM WITH MgO

Property	Before Heat Treatment	After 98 hours in Vacuum In Contact with MgO	 No Ceramic Contact
Surface hardness, VPN 2.5 kg	230	612	250
Core hardness, VPN 2.5kg	230	503	250
Bend transition temperature, °C	<20	1100+	<20
Electrical resistivity, microhm-cm	17.5	59.2(a)	18.1

(a) After 21 hours.

c. Boron Nitride

Studies of 90Ta-10W interations with boron nitride were carried out under nitrogen, helium, and vacuum for up to 98 hours at 1500°C.

(1) (90Ta-10W)-BN under Nitrogen

Four exposures at 1500°C, each of 5 hours' duration, were made using varying nitrogen flow rates. In all cases, the surface hardness values were in the VPN 1400-1600 range for samples in contact with boron nitride and also for the control specimens which were not in contact with the ceramic material. The microstructures did not contain the boride surface layer, but traces of a fine acicular precipitate were noted, especially in the slow-cooled specimens. It is apparent that hardening of the surface is primarily due to nitrogen.

(2) (90Ta-10W)-BN under Helium

Interactions between boron nitride and the 90Ta-10W alloy were carried out at 1500°C under a helium atmosphere. After 21 hours, the hardness of the core increased only slightly to VPN 268. Variable surface hardness readings were obtained; some areas of the surface were below VPN 300 while other areas were above VPN 1000. Metallographic examination revealed that the hard surface compound, probably a boride, had formed in small areas which covered approximately one half of the surface. These results indicate that the compound was formed mainly at the points of contact between boron nitride granules and the alloy surface. The 90Ta-10W alloy appears to be more compatible with boron nitride under an inert atmosphere than under vacuum. Under both atmospheres, the alloy reacts more slowly with boron nitride than does unalloyed tantalum.

(3) (90Ta-10W)-BN under Vacuum

Specimens of the 90Ta-10W alloy were embedded in boron nitride and heated for 98 hours at 1500°C under vacuum. Surface hardness levels rose rapidly, reaching values of VPN 1288 after 21 hours and 1782 after 49 hours. The core hardness rose to VPN 488 after 7 hours but remained essentially unchanged during the remaining 91 hours. Only a slight increase in electrical resistivity was measured after 98 hours. (19.3 to 21.8 microhm-cm).

The microstructure showed a single phase core with a thin (0.005 inch) surface layer of somewhat columnar grains of the very hard compound, probably a complex boride. Bend test results showed brittle fracture at 800°C, but a ductile bend was observed at 1100°C. The latter sample had numerous cracks in the thin surface layer, but these cracks did not propagate during the bend test. Property data for the 90Ta-10W alloy in boron nitride under vacuum at 1500°C are summarized in Table XII.

TABLE XII

ROOM-TEMPERATURE PROPERTIES OF 90Ta-10W AFTER 98 HOURS AT 1500°C IN VACUUM WITH BN

Property	Before Heat Treatment	After 98 hours in Vacuum In Contact with BN	After 98 hours in Vacuum No Ceramic Contact
Surface hardness, VPN 2.5kg	230	1850+	250
Core hardness, VPN 2.5kg	230	485	250
Bend transition temperature, °C	<20	~1000	<20
Electrical resistivity, microhm-cm	17.5	21.8	18.1

d. Beryllia Oxide

The 90Ta-10W alloy was heated in contact with beryllia for 10 hours at 1500°C under a highly purified argon atmosphere. No changes in surface and core hardness were measured, and there was no indication of a surface reaction.

4. Molybdenum

Unalloyed molybdenum was included in these studies primarily to compare its compatibility with ceramics with that of the commercial molybdenum alloy TZM.

a. Alumina

Molybdenum-alumina interactions were studied at 1500°C under hydrogen and nitrogen atmospheres.

(1) Mo-Al_2O_3 under Hydrogen

Previous studies at IITRI have shown that molybdenum could be embrittled by heating in contact with Al_2O_3 under a hydrogen atmosphere.(4) This early work utilized alumina powder of about 99.5 per cent purity, a grade similar to Agsco No. 36; it was found that the ductile-to-brittle transition temperature was increased from near 0°C to about 100°C by a 1-hour exposure at 1500°C.

Interaction studies under this program utilized the very high purity RS-17 alumina and also the Agsco No. 36 material. Molybdenum specimens were embedded in the powdered alumina and heated to 1500°C for 5 hours at 1500°C. Surface hardness and transverse-rupture strength values were virtually the same for samples heated in contact with both grades of oxides; similar results were obtained for the control specimens which were wrapped in molybdenum foil. It is possible that the newer molybdenum used on this program had a lower ductile-to-brittle transition temperature, so that any increase which occurred was still below room temperature. Sufficient samples were not available to explore transition behavior at lower temperatures.

(2) Mo-Al_2O_3 under Nitrogen

Very little change in surface and core hardness occurred when molybdenum was heated in contact with alumina under varying flow rates of nitrogen for 10 hours at 1500°C. There was no metallographic evidence of surface compounds or other phases in the molybdenum matrix.

There are two well established nitrides of molybdenum--Mo_2N and MoN. Molybdenum can be nitrided most readily by contact with ammonia at 400° to 725°C; at higher temperatures the nitrides tend to dissociate.(5) It is possible to nitride molybdenum powder by treating with nitrogen at 800°C.(6) The absence of nitride formation during these interaction studies may be attributed to the instability of the nitrides at the 1500°C temperature used.

b. Magnesia

Unalloyed molybdenum was heated in contact with magnesia at 1500°C under hydrogen and nitrogen atmospheres.

(1) Mo-MgO under Hydrogen

Molybdenum specimens embedded in magnesia were heated for 5 hours at 1500°C under a hydrogen atmosphere. Surface hardness values of these specimens were VPN 191-198, and modulus of rupture strengths were near 107, 000. Similar results were obtained for the control specimens which had been wrapped in molybdenum foil to prevent contact with magnesia. Based on this short-time exposure, molybdenum appears to be relatively inert in contact with magnesia under hydrogen.

(2) Mo-MgO under Nitrogen

Four exposures of 5 hours each at 1500°C, using varying nitrogen flow rates, were made with molybdenum specimens embedded in magnesia. Surface and core hardness values were VPN 188 to 193, as were the control specimens. No evidence of surface interaction was noted in the microstructures.

c. Boron Nitride

Molybdenum-boron nitride interactions were studied on specimens exposed at 1500°C under hydrogen and nitrogen atmospheres.

(1) Mo-BN under Hydrogen

Molybdenum specimens heated in contact with boron nitride for 5 hours under hydrogen at 1500°C had surface hardnesses in the VPN 1000-1475 range, whereas the control specimen was near VPN 200. The thin boride layer apparently strengthened the metal, as the transverse-rupture strength was 131,000 psi compared to 107,000 psi for the control specimen. These results indicate that molybdenum is excessively hardened in very short times by contact with boron nitride under hydrogen at 1500°C.

(2) Mo-BN under Nitrogen

Surface hardening of molybdenum in contact with boron nitride under nitrogen appeared to be related to the availability of nitrogen at the metal surface. When high flow rates of nitrogen were used, very little hardening was noted, especially on the upper surfaces of the metal specimens. At low nitrogen flow rates, and on metal surfaces which were well beneath the top of the boron nitride layer, a number of hard spots were formed on the molybdenum surfaces.

d. Beryllia

Molybdenum heated in contact with beryllia for 10 hours at 1500°C under argon did not exhibit an increase in surface or core hardness. The microstructures were clean, and no evidence of surface reactions were observed.

5. Molybdenum Alloy TZM

The commercial TZM alloy, Mo-0.5Ti-0.08Zr, has a much higher recrystallization temperature than unalloyed molybdenum; its elevated temperature strength properties are greatly superior to those of the pure metal. TZM interaction studies encompassed all of the ceramic materials and atmospheres investigated under this program.

a. Alumina

Interactions between TZM and alumina were conducted under hydrogen, nitrogen, and vacuum for up to 98 hours at 1500°C.

(1) TZM-Al_2O_3 under Hydrogen

TZM specimens were embedded in alumina and heated for 10 hours at 1500°C. Surface hardness values were similar to those obtained for the control specimens. Modulus of rupture values were also nearly identical, and all specimens had ductile bends at room temperature. No evidence of surface reactions was noted in the microstructure, although a thin layer (0.005 inch) of unrecrystallized grains was evident at the surfaces of all specimens. Surface hardness values of VPN 270 were somewhat higher than normal for annealed TZM. The higher hardness of the surface layer may be due to reaction of hydrogen, or reaction of impurities such as oxygen or nitrogen in the furnace atmosphere, with the titanium and zirconium in the molybdenum alloy.

(2) TZM-Al_2O_3 under Nitrogen

The TZM-alumina interactions were carried out for 5 and 10 hours at 1500°C using different flow rates of nitrogen. All specimens, including those wrapped in molybdenum foil to prevent contact with alumina, had surface hardnesses in the range of VPN 390 to 500. Core hardness values were VPN 215, indicating that no hardening had occurred. The microstructures consisted of a layer of unrecrystallized grains which extended to depths of 0.010 to 0.015 inch below the surface, while the core was fully recrystallized.

Thus the surface hardening and absence of surface recrystallization may be attributed to the nitrogen, rather than to contact with alumina. The hardening mechanism is assumed to be the formation of an ultrafine dispersion of titanium and zirconium nitrides in the molybdenum matrix. A similar mechanism has been reported for the Mo-0.5Ti alloy where surface hardnesses were doubled after exposing the alloy to nitrogen for 27 hours at temperatures up to 1500°C.(7)

(3) TZM-Al_2O_3 under Vacuum

Interaction studies of TZM in contact with Al_2O_3 were conducted for 98 hours under vacuum at 1500°C. Virtually no changes in surface and core hardness were measured after the 98-hour exposure.

Electrical resistivity varied slightly from 6.5 to 7 microhm-cm. The ductile-to-brittle transition temperature was between room temperature and 200°C, indicating that a very slight increase had occurred. The microstructures were clean, with no evidence of compounds or surface layers. Thus TZM appears to be very compatible with alumina under vacuum at 1500°C, as shown in Table XIII.

TABLE XIII

ROOM-TEMPERATURE PROPERTIES OF TZM ALLOY AFTER 98 HOURS AT 1500°C UNDER VACUUM IN Al_2O_3

Property	Treatment	After 98 hours in Vacuum: In Contact with Al_2O_3	After 98 hours in Vacuum: No Ceramic Contact
Surface hardness, VPN 2.5kg	205	206	206
Core hardness, VPN 2.5kg	205	200	203
Bend transition temperature, °C	<20	~100	<20
Electrical resistivity, microhm-cm	6.7	7.0	6.8

b. Magnesia

TZM-magnesia interaction studies were carried out under hydrogen, nitrogen, and vacuum at 1500°C.

(1) TZM-MgO under Hydrogen

Specimens of the molybdenum alloy TZM were embedded in magnesia and heated for 5 hours under hydrogen at 1500°C; control specimens wrapped in molybdenum foil were also included in the same furnace run. Ductile bends and similar strengths were obtained on all specimens. The surface hardness levels of the samples embedded in magnesia and also the control specimens were near VPN 270, while the core hardness was VPN 205-210. These surface hardness values are somewhat high for TZM. It was found that a surface layer of grains approximately 0.005 inch thick was not recrystallized, while the core was completely recrystallized in all specimens. The increased hardness may possibly be due to compound formation by the reactive metal constituents titanium and zirconium in the alloy. While hydride formation may be possible, it appears more likely that oxygen and/or nitrogen impurities in the hydrogen atmosphere were responsible.

(2) TZM-MgO under Nitrogen

Results for the TZM-magnesia interactions were nearly identical to those reported above for TZM-alumina under nitrogen. All specimens including the control samples exhibited a hard layer of unrecrystallized grains which extended 0.010 to 0.015 inch below the surface. This layer had hardness levels in the VPN 390 to 525 range. The core consisted of fully recrystallized grains. Thus the surface hardening is due to nitrogenation of the reactive metal constituents titanium and zirconium in the alloy.

(3) TZM-MgO under Vacuum

TZM specimens embedded in MgO were heated under vacuum for 98 hours at 1500°C. While the core hardness remained virtually constant at VPN 205, the surface hardness increased moderately from an initial value of 6.7 to a value of 8.7 microhm-cm after 98 hours. The microstructures consisted of fully recrystallized alloy grains with no evidence of precipitates or surface reactions. However, the grain size was somewhat finer near the surface than at the center of the specimens.

A very slight increase in ductile-to-brittle transition temperature occurred after 98 hours. Whereas the control specimen was ductile at room temperature, the specimens heated in contact with magnesia were brittle at room temperature but were ductile at 200°C. Table XIV shows that TZM is relatively compatible with MgO under vacuum at 1500°C, but not as compatible as the TZM-Al_2O_3 combination (Table XIII).

TABLE XIV

ROOM-TEMPERATURE PROPERTIES OF TZM ALLOY AFTER 98 HOURS AT 1500°C UNDER VACUUM IN MgO

Property	Before Heat Treatment	After 98 hours in Vacuum In Contact with MgO	 No Ceramic Contact
Surface hardness, VPN 2.5kg	205	251	206
Core hardness, VPN 2.5kg	205	205	203
Bend transition temperature, °C	<20	~100	<20
Electrical resistivity, microhm-cm	6.7	8.7	6.8

c. Boron Nitride

TZM-boron nitride interactions were carried out at 1500°C under hydrogen, nitrogen, and vacuum.

(1) TZM-BN under Hydrogen

After 5 hours in hydrogen at 1500° C, the TZM specimens had surface hardness values in the VPN 802-974 range, and the modulus of rupture was 88,000 psi compared to 114,000 psi for the control specimen. Furthermore, the specimen embedded in boron nitride exhibited brittle failure, whereas the control sample had a ductile bend. A very thin (0.001 inch) layer of the hard boride compound was found on the exposed surfaces.

(2) TZM-BN under Nitrogen

Specimens of TZM embedded in boron nitride were heated for 5 and 10 hours at 1500°C using varying nitrogen flow rates. All specimens, including the control samples, were surface hardened to approximately VPN 405-440. While the majority of specimens in contact with boron nitride did not exhibit the hard boride surface layer, one sample heated in static nitrogen had a few small areas of this compound on the surface.

(3) TZM-BN under Vacuum

Interactions between TZM and boron nitride were carried out for 98 hours at 1500°C under vacuum. The surface hardness rose to a value of VPN 1003 after 49 hours, and measurements could not be obtained after 98 hours because of the rough, cracked surface. Core hardness remained virtually constant in the VPN 205-211 range. Electrical resistivity rose slowly from near 7 microhm-cm to a value of 7.8 microhm-cm after 98 hours. A thin layer, 0.005 inch deep, of the hard compound was present on the exposed surfaces, while the core consisted of recrystallized alloy grains. In spite of the hard surface layer, the 98-hour specimens were ductile at 200°C. However, brittle fracture at a very low stress level was obtained at room-temperature. Pertinent property data are summarized in Table XV.

TABLE XV

ROOM-TEMPERATURE PROPERTIES OF TZM ALLOY AFTER 98 HOURS AT 1500°C UNDER VACUUM IN BN

Property	Before Heat Treatment	After 98 hours in Vacuum	
		In Contact with BN	No Ceramic Contact
Surface hardness, VPN 2.5kg	205	1000+	206
Core hardness, VPN 2.5kg	205	208	203
Bend transition temperature, °C	<20	~100	<20
Electrical resistivity, microhm-cm	6.7	7.8	6.8

d. Beryllia

The alloy TZM was heated in contact with beryllia for 10 hours at 1500°C under an argon atmosphere. As in the case of the other metal specimens exposed to beryllia, TZM was not hardened, nor were any structural changes observed in the microstructures. On the basis of this short-time exposure, TZM and beryllia appear to be compatible.

C. General Comments on Results

1. Comparative Data

The previous sections have presented separately the results of experimental work on various combinations of metals, ceramics, and atmospheres. This section of the report compares data for these combinations so that an order of merit may be established for compatibility or degree of interaction.

a. 98-hour 1500°C Exposure

Specimens of tungsten, tantalum, 90Ta-10W, and the molybdenum alloy TZM were heated in contact with alumina, magnesia, and boron nitride for 98 hours in vacuum at 1500°C. Comparative data for surface and core hardness for the various metals indicate that some metal-ceramic combinations are unsuitable after elevated-temperature contact for 98 hours. Figures 68 through 71 present surface hardness data for the metal specimens after heating in contact with the various ceramics. The surface hardness of tungsten was increased only by contact with boron nitride (Figure 68). Tantalum was excessively hardened by contact with boron nitride, and was moderately hardened by alumina and magnesia contact (Figure 69). Similar results were obtained for the 90Ta-10W alloy (Figure 70). The molybdenum alloy TZM behaved similarly to tungsten in that it was surface hardened only by contact with boron nitride (Figure 71).

Core hardness data for the same combinations are presented in Figures 72 through 75. It may be seen that tungsten (Figure 72) and TZM (Figure 75) had relatively unchanged core hardness values, whereas core hardness of tantalum (Figure 73) and 90Ta-10W (Figure 74) was increased by contact with all of the ceramic materials.

Table XVI summarizes the change in bend transition behavior for the various metals after contact with alumina, magnesia, and boron nitride for 98 hours at 1500°C under vacuum.

TABLE XVI

BEND TRANSITION DATA FOR METAL SPECIMENS AFTER CONTACT WITH CERAMICS FOR 98 HOURS AT 1500°C

Metal	Ceramic	Bend Transition Temperature, °C Before Contact	Bend Transition Temperature, °C After Contact
Tungsten	Al_2O_3	~300	<400
	MgO	~ 300	< 400
Tantalum	Al_2O_3	subzero	600
	MgO	subzero	~1000
	BN	subzero	1100+
90Ta-10W	Al_2O_3	<20	1100+
	MgO	<20	1100+
	BN	<20	~1000
TZM	Al_2O_3	<20	~100
	MgO	<20	~ 100
	BN	<20	~100

These data indicate that the bend transition temperature of tungsten and TZM were little affected by the 98-hour contact with the various ceramics, while the more reactive tantalum and 90Ta-10W were severely embrittled.

b. Other Exposures

The same combinations of metals and ceramics were exposed for 21 hours at 1500°C under a helium atmosphere. In general, the surface and core hardness data were similar to those shown for the vacuum run. Exposures were also made under hydrogen and nitrogen for most of the metal-ceramic combinations. While most of these exposures were of relatively short-time duration (10 to 20 hours), severe property degradations were noted for many of the metal specimens. Tables XVII through XXI summarize the relative degree of compatibility of the metals after contact with the various ceramic materials under hydrogen, nitrogen, vacuum, or inert atmosphere. Data for beryllia are omitted in these tables because no evidence of interaction was found for any of the combinations after 10 hours under argon at 1500°C.

In general, tungsten, molybdenum, and the molybdenum alloy TZM were quite compatible with alumina and magnesia under hydrogen, vacuum, and inert gas. However, these materials reacted with boron nitride except during short exposures under flowing nitrogen. The unalloyed metals did not react with nitrogen, whereas the alloy TZM was excessively hardened by elevated-temperature treatment in nitrogen. This hardening was due to the presence of the reactive metals titanium and zirconium which probably formed nitrides. The alloy TZM also appeared to react slightly with hydrogen; this effect should be more thoroughly explored. Thus the Group VI B materials with their relatively low reactivity and their very low solubility for the interstitials oxygen, nitrogen, and hydrogen appear to be better suited for long-time elevated-temperature exposures under the range of conditions investigated under this program.

TABLE XVII

RELATIVE COMPATIBILITY DATA FOR TUNGSTEN

	Atmosphere		
Ceramic	Hydrogen	Nitrogen	Inert or Vacuum
Al_2O_3	Slight strength loss with applied DC voltage after 4 hrs at 1500°C; no property changes without applied voltage.	Very slight strength loss after 10 hrs at 1500°C; hardness, structure unchanged.	Virtually no property changes after 98 hrs in vacuum or 21 hrs in helium at 1500°C.
MgO	Virtually no property changes with or without applied voltage after 4 hrs at 1500°C.	No changes in surface or core hardness after 10 hrs at 1500°C.	No changes in mechanical properties after 98 hrs at 1500°C; slight increase in resistivity.
BN	Surface hardness increased to VPN 630 after 4 hrs at 1600°C; strength loss exceeded 50 per cent.	Hardness unchanged after 20 hrs at 1500°C in flowing N_2; surface hardness increased under static N_2.	Severe loss of strength (75 per cent) and high surface hardness (VPN 1800+) after 98 hrs in vacuum. Surface hardened after 21 hrs in helium

TABLE XVIII

RELATIVE COMPATIBILITY DATA FOR TANTALUM

Ceramic	Atmosphere		
	Hydrogen	Nitrogen	Inert or Vacuum
Al_2O_3	Not tested because of known hydride formation.	Surface excessively hardened primarily by nitrogen absorption after 10 hrs at 1500°C.	Hardness increased to VPN 690, and bend transition temperature increased to 600°C after 98 hrs at 1500°C.
MgO	Not tested because of known hydride formation.	Surface excessively hardened primarily by nitrogen absorption after 10 hrs at 1500°C.	Hardness increased to VPN 440, and bend transition temperature increased to near 1000°C after 98 hrs at 1500°C in vacuum.
BN	Not tested because of known hydride formation.	Surface excessively hardened by nitrogen absorption after 10 hrs at 1500°C in flowing N_2. Hard surface compound formed in static N_2.	High surface hardness (VPN 1850+) and high bend transition temperature (1100°C+) after 98 hrs at 1500°C in vacuum.

TABLE XIX

RELATIVE COMPATIBILITY DATA FOR 90Ta-10W

Ceramic	Atmosphere Hydrogen	 Nitrogen	 Inert or Vacuum
Al_2O_3	Not tested because of known hydride formation.	Very high surface hardness (VPN 1500+) because of nitrogen absorption after 10 hrs at 1500°C.	Hardness increased to VPN 620, and bend transition temperature increased to 1100°C+ after 98 hrs at 1500°C in vacuum.
MgO	Not tested because of known hydride formation.	Very high surface hardness (VPN 1500+) because of nitrogen absorption after 10 hrs at 1500°C.	Hardness increased to VPN 500 (core) and 612 (surface) and bend transition temperature increased to 1100°C+ after 98 hrs at 1500°C in vacuum.
BN	Not tested because of known hydride formation.	Very high surface hardness (VPN 1400+) because of nitrogen absorption after 10 hrs at 1500°C in flowing N_2.	Surface hardness increased to VPN 1850+, and bend transition was near 1000°C after 98 hrs at 1500°C in vacuum.

TABLE XX

RELATIVE COMPATIBILITY DATA FOR MOLYBDENUM

Ceramic	Atmosphere Hydrogen	 Nitrogen	 Inert or Vacuum
Al_2O_3	No change in strength or hardness after 5 hrs at 1500°C, using 99.9 per cent purity Al_2O_3.	No change in surface or core hardness after 10 hrs at 1500°C.	Not tested
MgO	No change in strength or hardness after 5 hrs at 1500°C.	No change in surface or core hardness after 10 hrs at 1500°C.	Not tested
BN	Surface hardness increased to VPN 1000-1475 after 5 hrs at 1500°C.	Very little surface hardening in flowing N_2; surface was hardened in static N_2.	Not tested

TABLE XXI

RELATIVE COMPATIBILITY DATA FOR TZM

Ceramic	Atmosphere		
	Hydrogen	Nitrogen	Inert or Vacuum
Al_2O_3	No change in strength after 5 hrs at 1500°C.	Surface was unrecrystallized and hardened to VPN 400-500 by internal nitrogenation after 10 hrs at 1500°C.	Virtually no hardness changes after 98 hrs in vacuum, or 21 hrs in helium at 1500°C; bend transition temperature increased slightly.
MgO	No change in strength after 5 hrs at 1500°C.	Surface was unrecrystallized and hardened to VPN 400-500 by internal nitrogenation after 10 hrs at 1500°C.	Surface hardness increased slightly to VPN 250, with slight increase in bend transition temperature after 98 hrs in vacuum.
BN	Surface hardness in creased to VPN 800-975 after 5 hrs at 1500°C.	Surface hardened to VPN 405-440 by internal nitrogenation after 10 hrs at 1500°C in flowing N_2. Some evidence of surface compound formation in static N_2.	Surface hardness was VPN 1000+, with slight increase in bend transition temperature after 98 hrs in vacuum at 1500°C

On the other hand, the more reactive metal titanium and the alloy 90Ta-10W exhibited reactions under all test conditions. These materials were hardened by nitrogen absorption in relatively short times, and they also formed hard surface compounds when heated in contact with boron nitride. In vacuum and under inert atmosphere they exhibited high hardnesses and greatly increased transition temperatures when heated in contact with alumina and magnesia. The exact nature of this hardening is not understood, but metallographic evidence indicates oxide formation and diffusion in the case of specimens heated in contact with magnesia. While heating in contact with alumina produced similar increases in hardness and transition temperature, no oxides were visible in the microstructures.

The increase in hardness to VPN 500-700 may be accounted for by solid solution of oxygen, and it is possible that the bend transition temperature could be increased to as high as 1100°C by this mechanism. This severe embrittlement of tantalum and 90Ta-10W under all combinations of ceramics and atmospheres makes these materials less attractive than tungsten or molybdenum for long-time elevated-temperature use. General comments for all of the combinations investigated are summarized in Table XXII (data for BeO are omitted because of limited test results).

c. Cesium Corrosion Survey

It had been planned to subject the various metal specimens to ceramic contact under a partial pressure of cesium vapor. A survey of the literature indicated that very elaborate precautions must be taken to completely exclude oxygen from the system so that any reactions could be attributed to the metal vapor rather than to the oxide of cesium. Some comments from the literature indicate that conflicting data have been obtained and that reactions with some of the refractory metals have been observed without contact with ceramics. M. J. Slivka studied the effects of exposure of 1 mm pressure of cesium vapor at 900°C for 281 hours on tantalum and molybdenum.(8) There was no evidence of reaction on the surface of molybdenum samples, whereas tantalum had internal pores and a precipitate near the surface. Studies at Vallecitos Atomic Laboratory

TABLE XXII

RELATIVE EFFECTS OF CERAMIC CONTACT AND ATMOSPHERE ON PROPERTIES OF METALS

Metal	Ceramic Material, 1500°C Interaction Temperature		
	Al_2O_3	MgO	BN
W	DC voltage across interface appears to reduce strength. Without applied voltage very little reaction under H_2 (4 hrs), N_2 (10 hrs), vacuum (98 hrs), or He (21 hrs).	Very little effect of applied DC voltage for 3 hrs in H_2. With no applied voltage, very little reaction under H_2 (3 hrs), N_2 (10 hrs) vacuum (98 hrs), or He (21 hrs).	Very hard surface layer formed in less than 10 hrs under H_2, vacuum, He, A, and static N_2; tendency for compound formation greatly reduced in flowing N_2.
Ta	Known to form hydrides; was excessively hardened by nitrogen absorption without ceramic contact. Embrittled by alumina contact after 98 hrs under vacuum.	Known to form hydrides; was excessively hardened by nitrogen absorption without ceramic contact. Embrittled by magnesia contact after 98 hrs in vacuum.	Known to form hydrides; was excessively hardened by nitrogen absorption without ceramic contact. Very hard surface layer formed after contact with BN after 98 hrs in vacuum.
90Ta-10W	Known to form hydrides; was excessively hardened by nitrogen absorption without ceramic contact. Embrittled by alumina contact after 98 hrs in vacuum for 21 hrs in helium.	Known to form hydrides; was excessively hardened by nitrogen absorption without ceramic contact. Severely embrittled by contact with magnesia after 98 hrs in vacuum or 21 hrs in helium.	Known to form hydrides; was excessively hardened by nitrogen absorption without ceramic contact. Severely embrittled by contact with BN after 98 hrs in vacuum or 21 hrs in helium.

TABLE XXII (continued)

Metal	Ceramic Material, 1500°C Interaction Temperature		
	Al_2O_3	MgO	BN
Mo	Possible increase in transition temperature in impure alumina under H_2. Not surface hardened in nitrogen at 1500°C for 10 hrs.	No property changes after 5 hrs in H_2 or 10 hrs in N_2.	Surface excessively hardened after 5 hrs in H_2 and in static N_2. Surface compound formation suppressed in flowing N_2.
TZM	Surface hardness slightly increased in H_2 (may be due to oxygen impurity in gas). Hardness increased in N_2 without ceramic contact. Very little reaction 98 hrs in contact with alumina in vacuum.	Surface hardness slightly increased in H_2 (may be due to oxygen impurity in gas). Hardness increased in N_2 without ceramic contact. Surface slightly hardened after 98 hrs in contact with magnesia in vacuum.	Surface excessively hardened after 5 hrs in H_2 and in nitrogen. Ver high surface hardness after 98 hrs in vacuum.

conducted at 1000°C under 20 torr cesium pressure showed no significant attack on tantalum after 235 hours.(9) This report also contains numerous references concerning cesium compatibility with various metals. A comprehensive bibliography of cesium corrosion is contained in a report issued under Contract AF 33(657)-10038 by the Bendix Corporation.(10)

Cesium often contains impurities which could markedly influence metal-ceramic compatibility data. Nitrogen, oxygen, and other gaseous contaminants were reported by Jensen.(11) The most profuse gaseous impurity in cesium is hydrogen, according to Johnson.(12) In a study by Hernqvist, it was found that some 170 micron-liters of hydrogen were evolved from 2 grams of cesium during a 12-hour operation of a cesium diode, and the evolution rate at the end of this time was still large.(13) The embrittling effects of hydrogen on tantalum are well known, and the presence of nitrogen is known to harden tantalum, 90Ta-10W, and TZM. It is thus recommended that any evaluation of metal-ceramic compatibility under a cesium atmosphere be undertaken only after purification of the cesium.

IV. ACKNOWLEDGMENTS

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V. LOGBOOKS

All data pertaining to work done in this period are recorded in IITRI Logbooks:

C-13810
C-13815
C-13816
C-13818
C-13880
C-14242
C-14328
C-14332
C-14334
C-14338
C-14344
C-14348
C-14392
C-14687
C-14788
C-14797
C-14799
C-14801
C-15250

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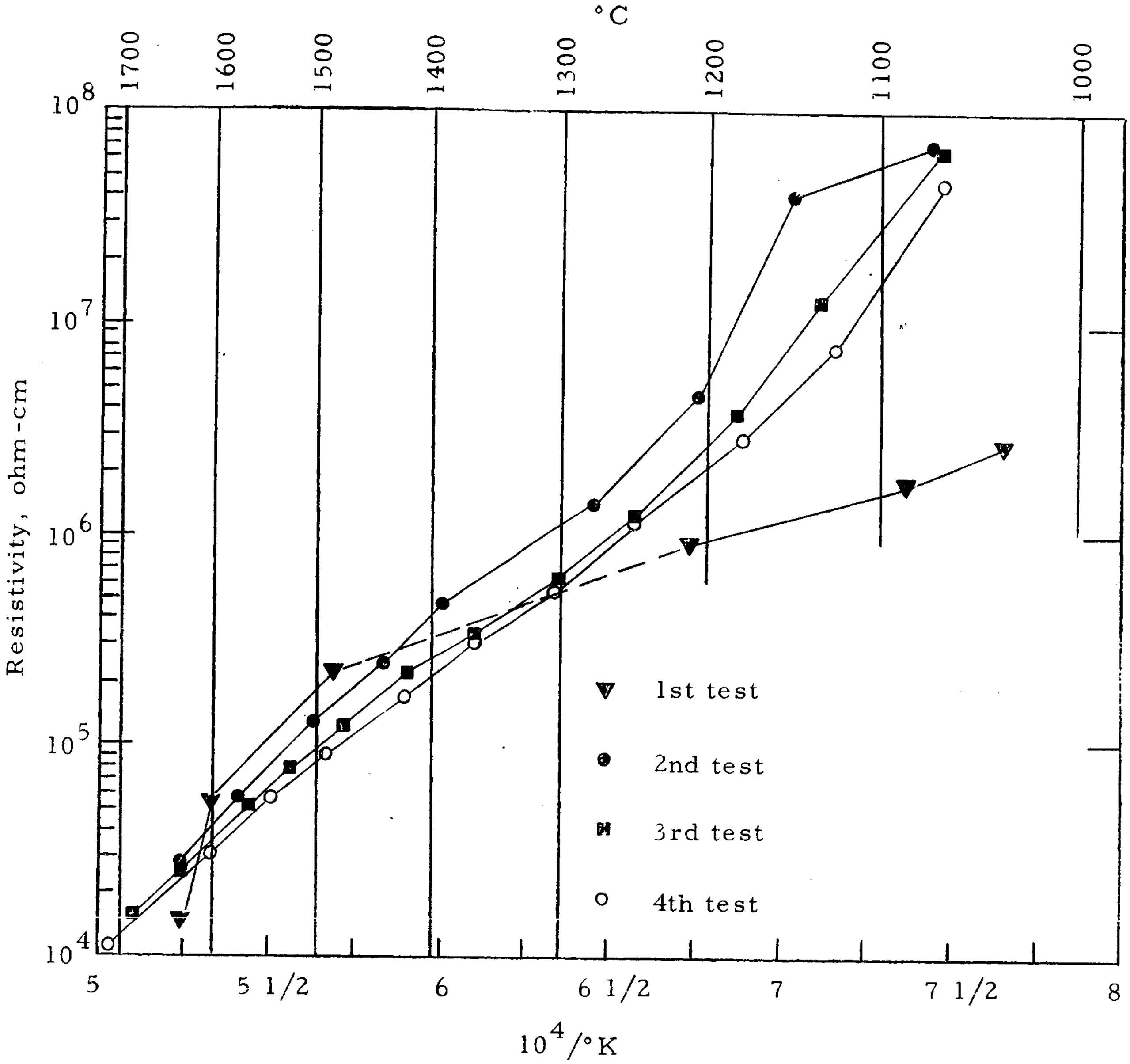


FIG. 1 - DC RESISTIVITY OF HIGH-PURITY ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN PREPURIFIED NITROGEN--SUMMARY OF HEATING CYCLE CURVES. Tungsten electrodes at 90 V. Graphite susceptor.

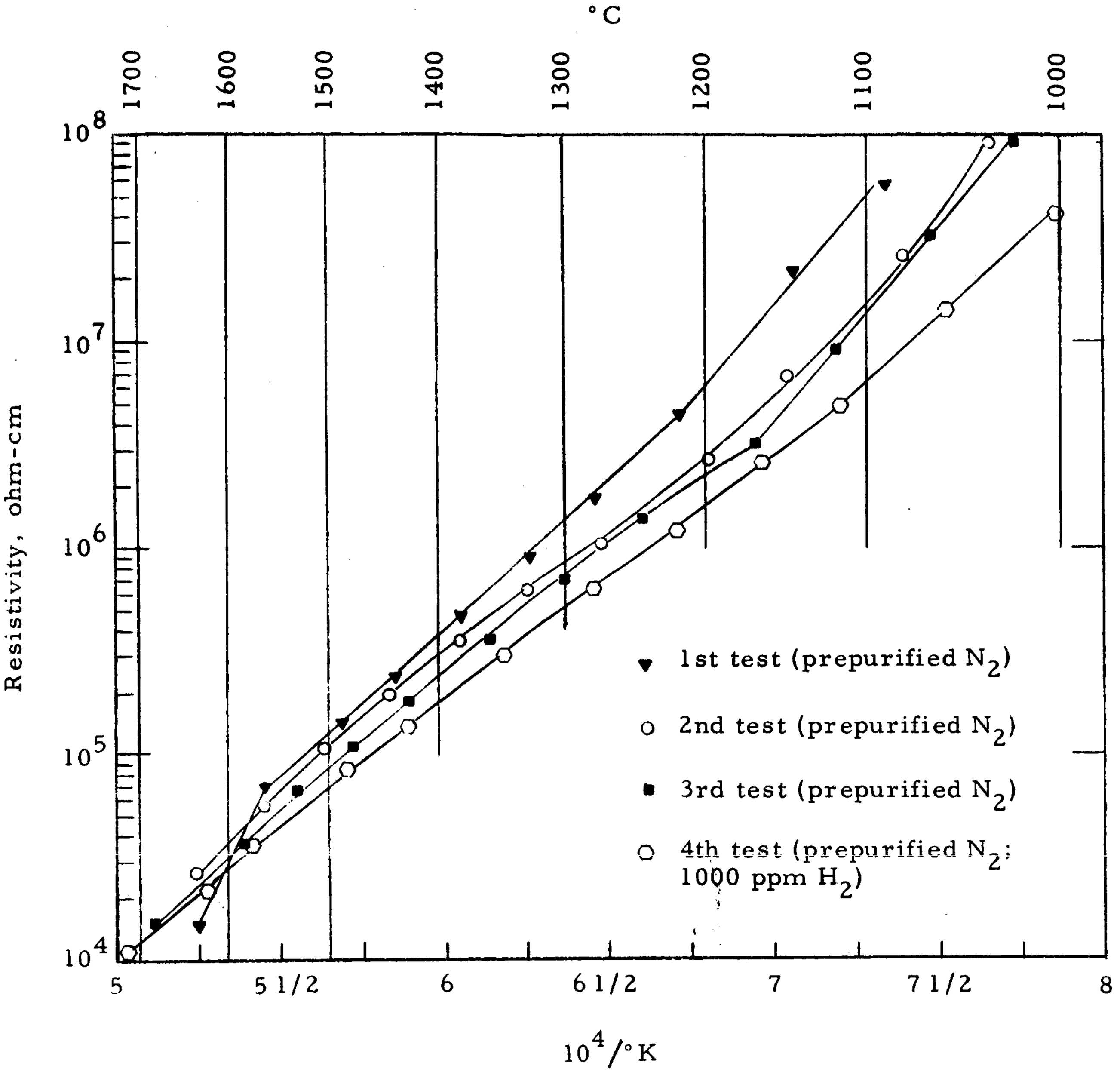


FIG. 2 - DC RESISTIVITY OF HIGH-PURITY ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN PREPURIFIED NITROGEN--SUMMARY OF COOLING CYCLE CURVES. Tungsten electrodes at 90V. Graphite susceptor.

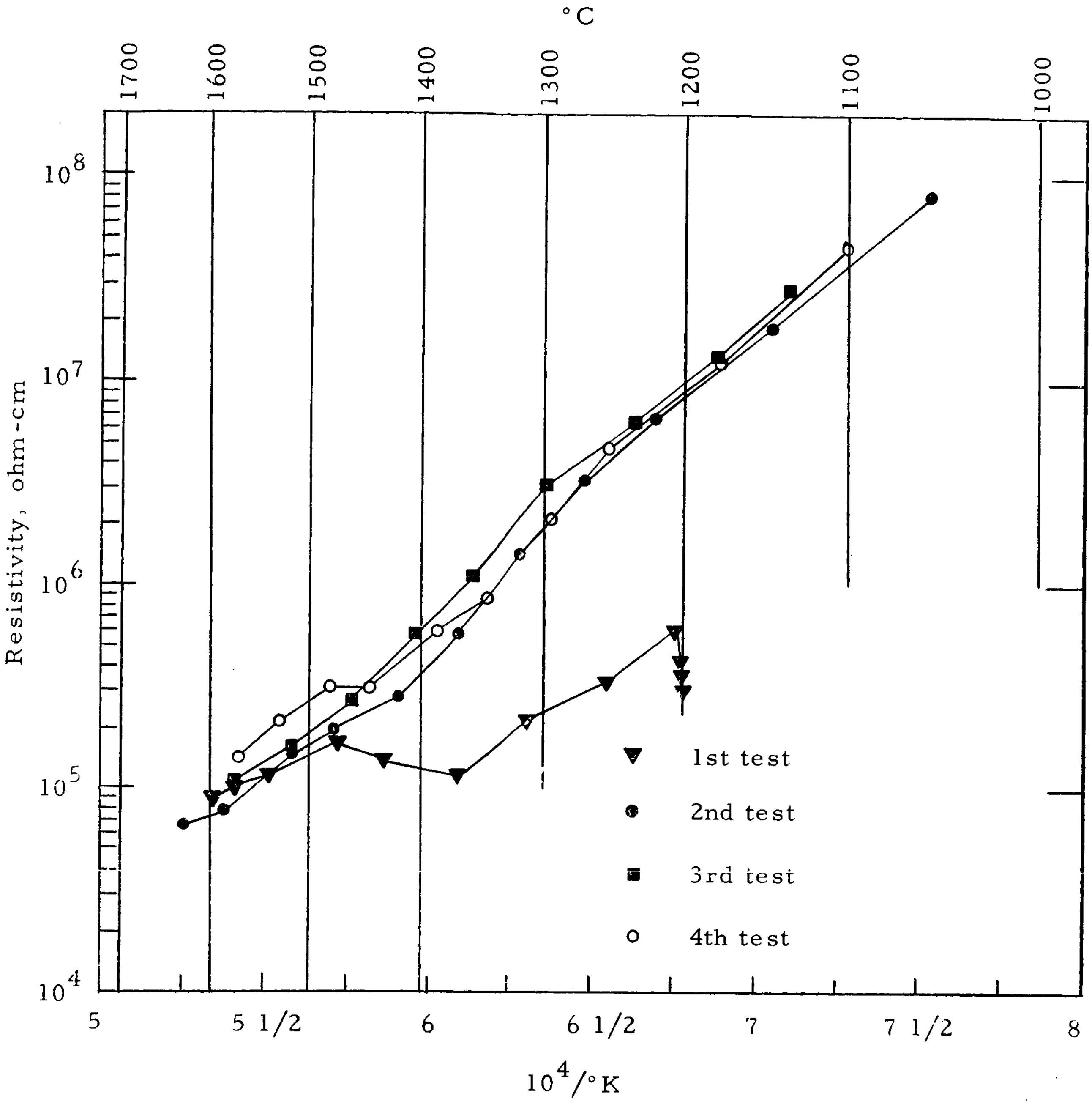


FIG. 3 - DC RESISTIVITY OF HIGH-PURITY ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN PREPURIFIED NITROGEN--HEATING CYCLE CURVES ON A TYPICAL SPECIMEN. Tungsten electrodes at 90V. Platinum susceptor.

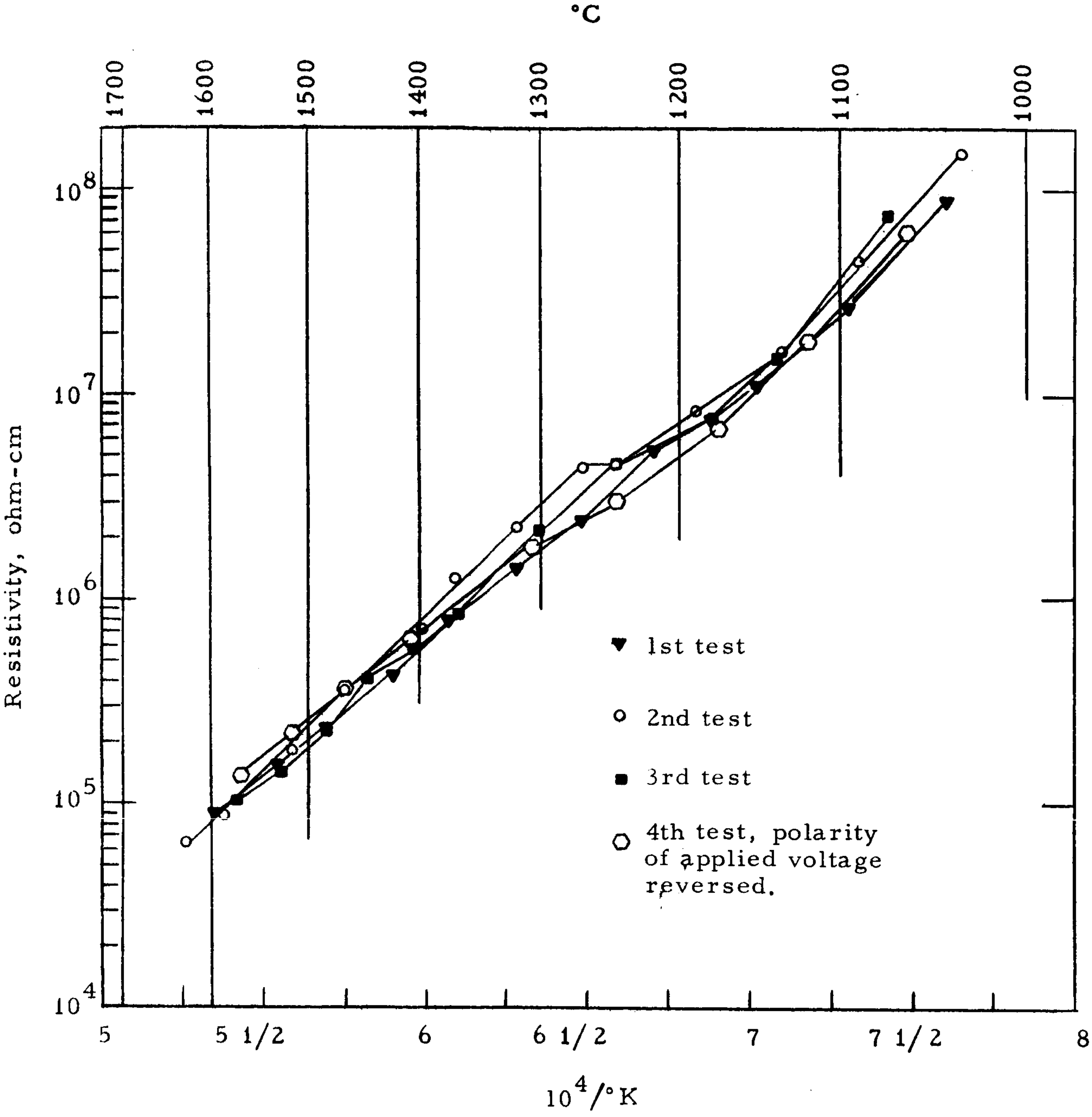


FIG. 4 - DC RESISTIVITY OF HIGH-PURITY ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN PREPURIFIED NITROGEN--SUMMARY OF COOLING CYCLE CURVES. Tungsten electrodes at 90 V. Platinum susceptor.

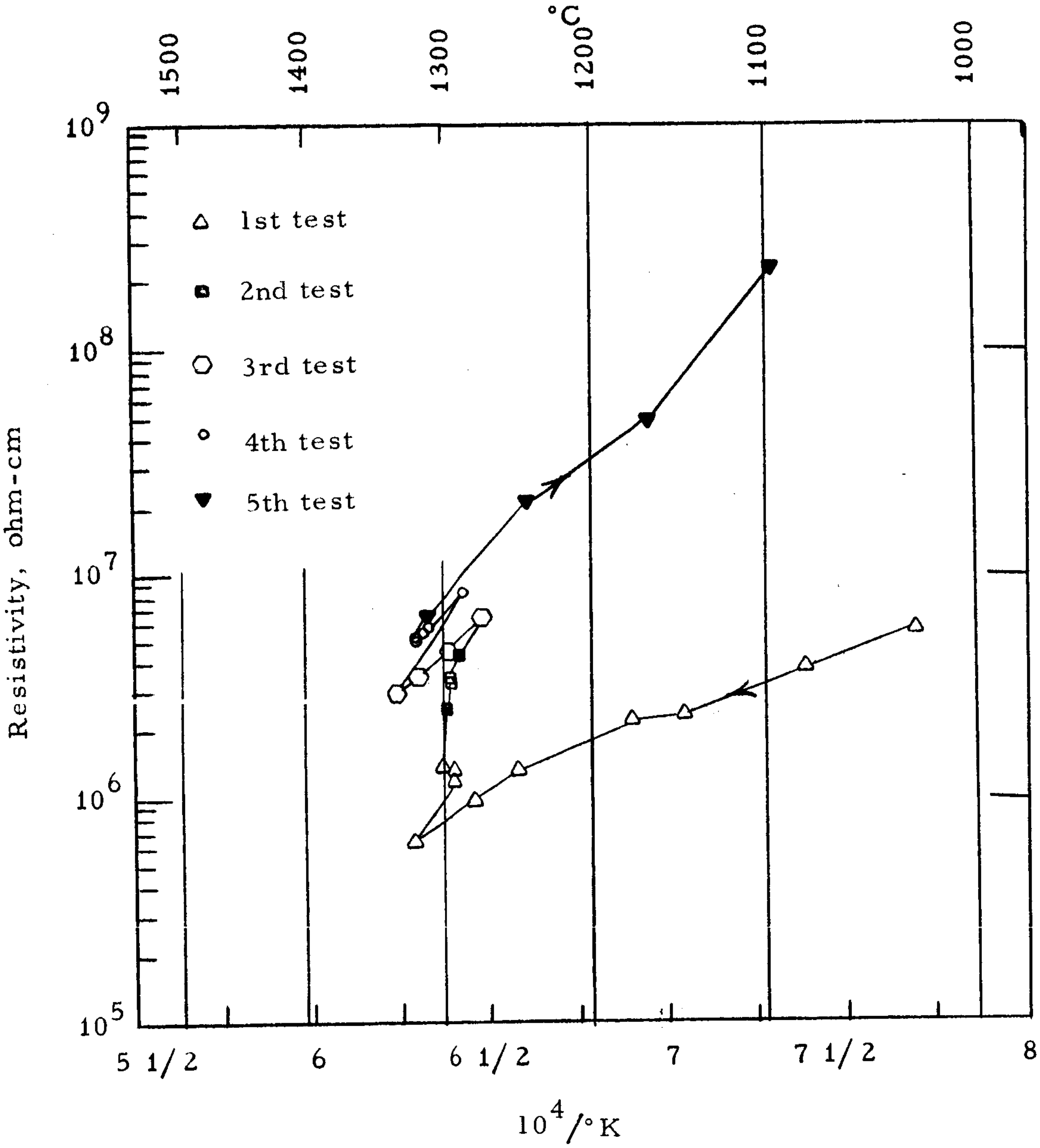
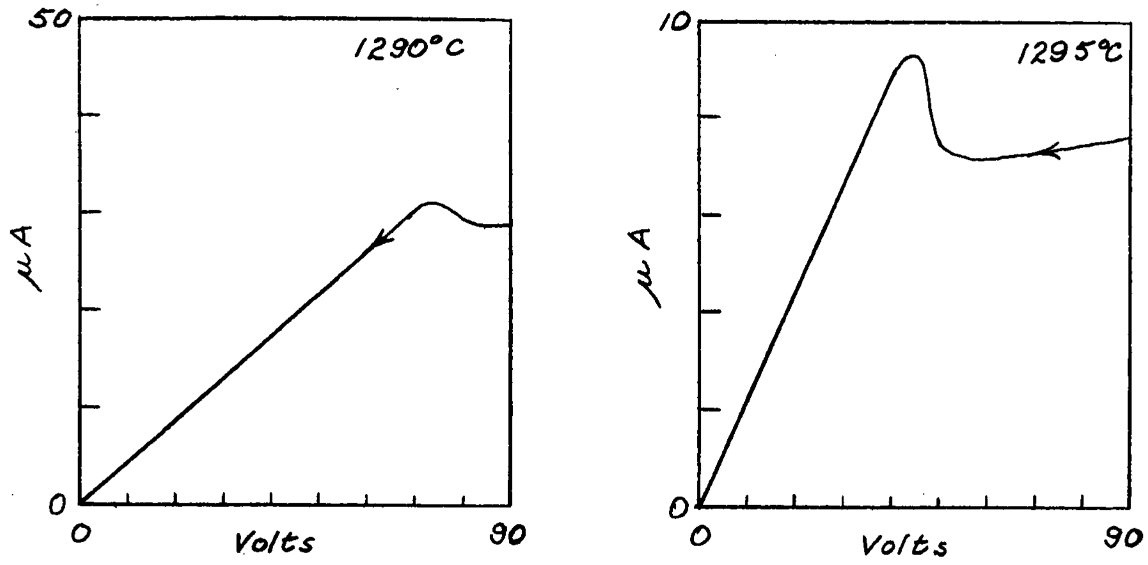
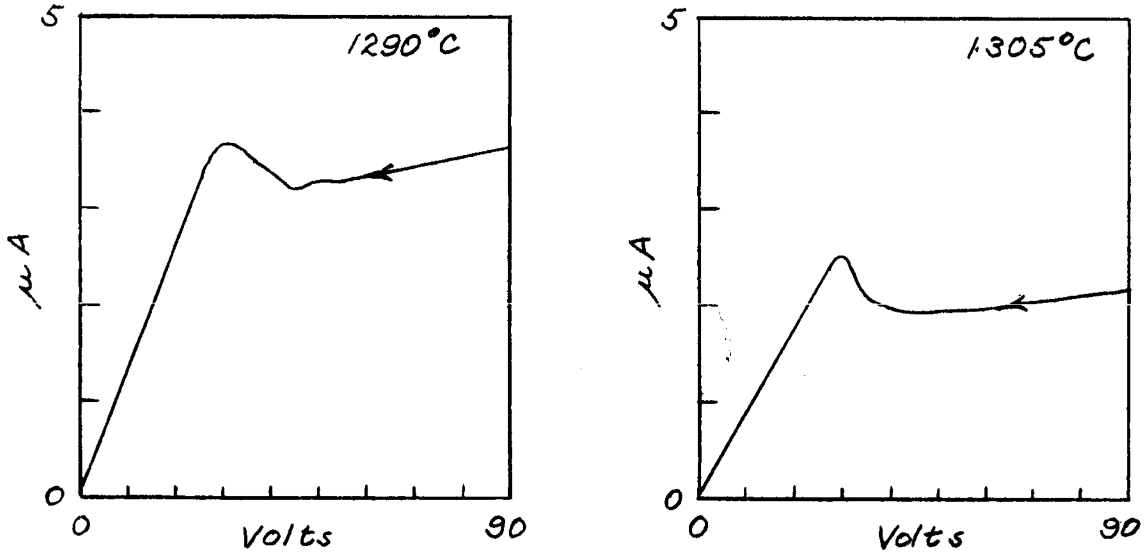


FIG. 5 - DC RESISTIVITY OF HIGH-PURITY ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN PREPURIFIED NITROGEN CONTAINING 1000 PPM HYDROGEN. 100-hour test. Tungsten electrodes at 90 V. Platinum susceptor.



a. 5 1/2 hours

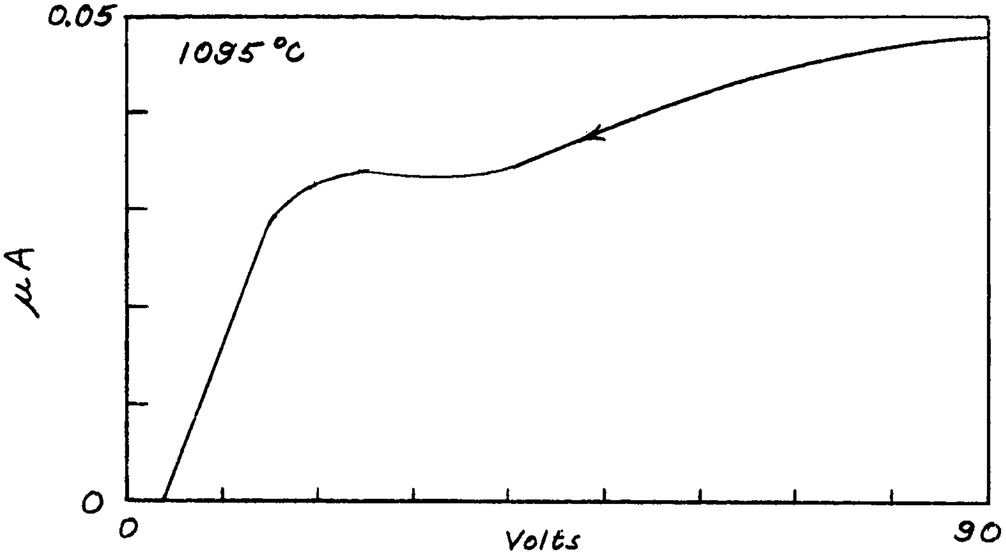
b. 24 hours



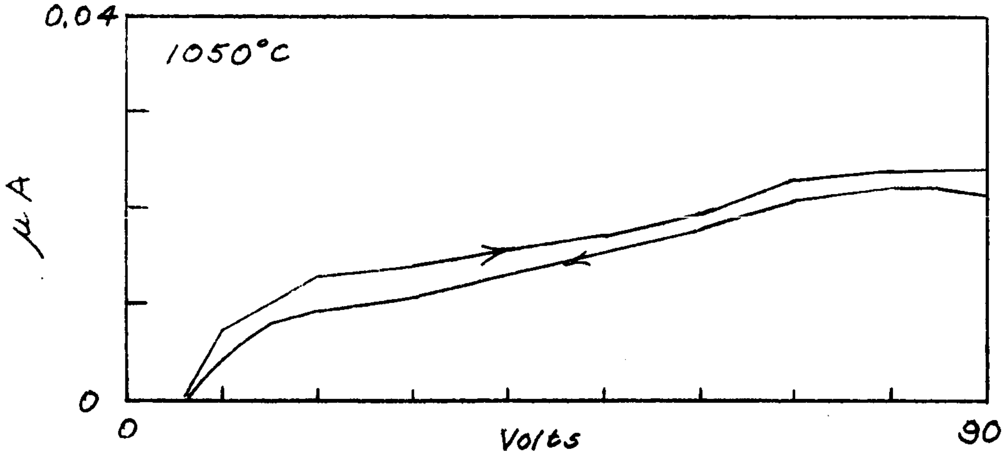
c. 49 hours

d. 96 hours

FIG. 6 - CURRENT VS. VOLTAGE AT 5 1/2, 24, 49, AND 96 HOURS FOR HIGH-PURITY ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN PREPURIFIED NITROGEN CONTAINING 1000 PPM HYDROGEN. Tungsten electrodes. Platinum susceptor.



a. 97 1/2 hours



b. 98 1/2 hours

FIG. 7 - CURRENT VS. VOLTAGE AT 97 1/2 AND 98 1/2 HOURS FOR HIGH-PURITY ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN PREPURIFIED NITROGEN CONTAINING 1000 PPM HYDROGEN. Tungsten electrodes. Platinum susceptor.

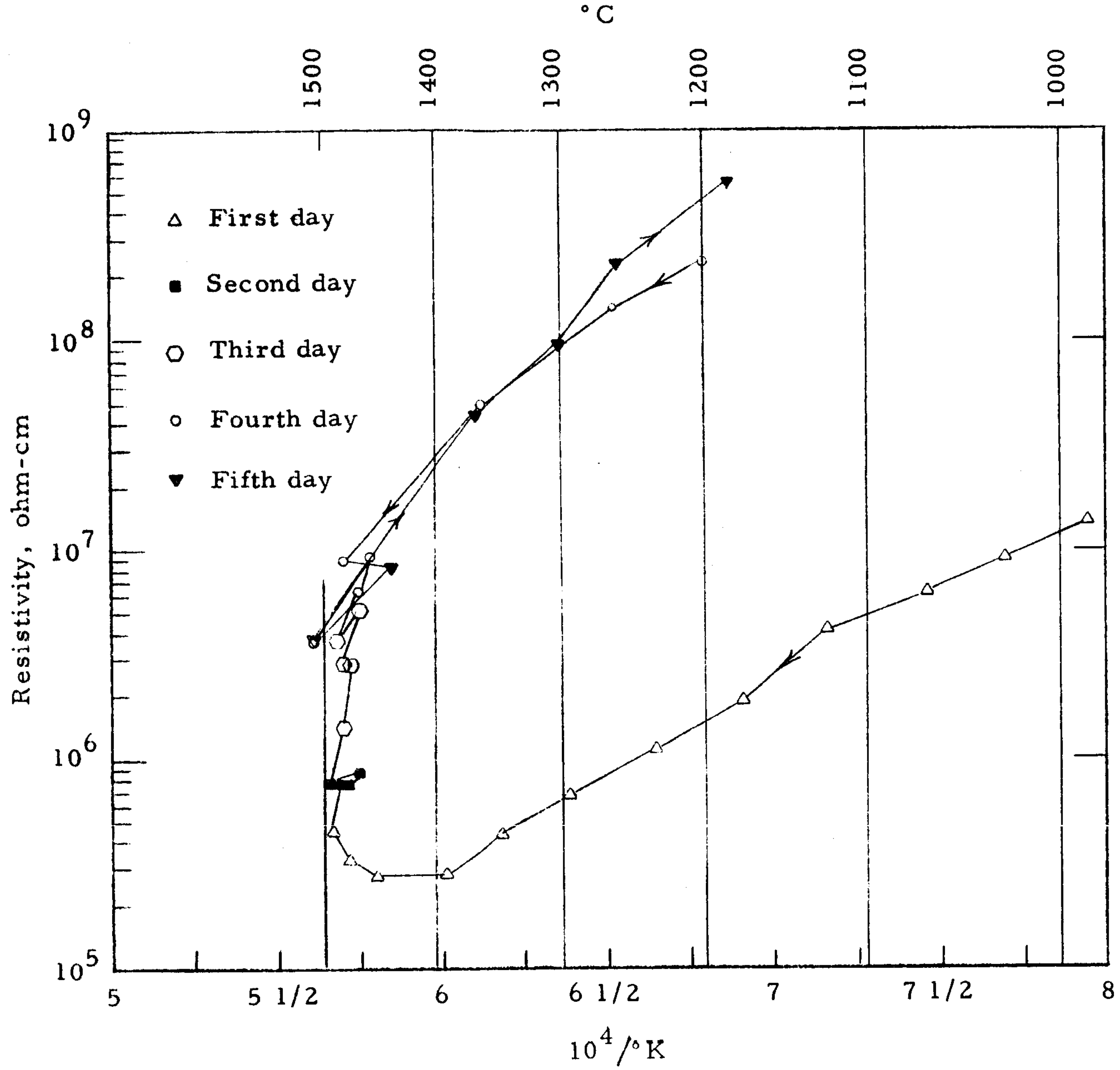


FIG. 8 - DC RESISTIVITY OF HIGH-PURITY ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN PREPURIFIED NITROGEN CONTAINING 1000 PPM HYDROGEN. 100-hour test. Tungsten electrodes at 90 V. Platinum susceptor.

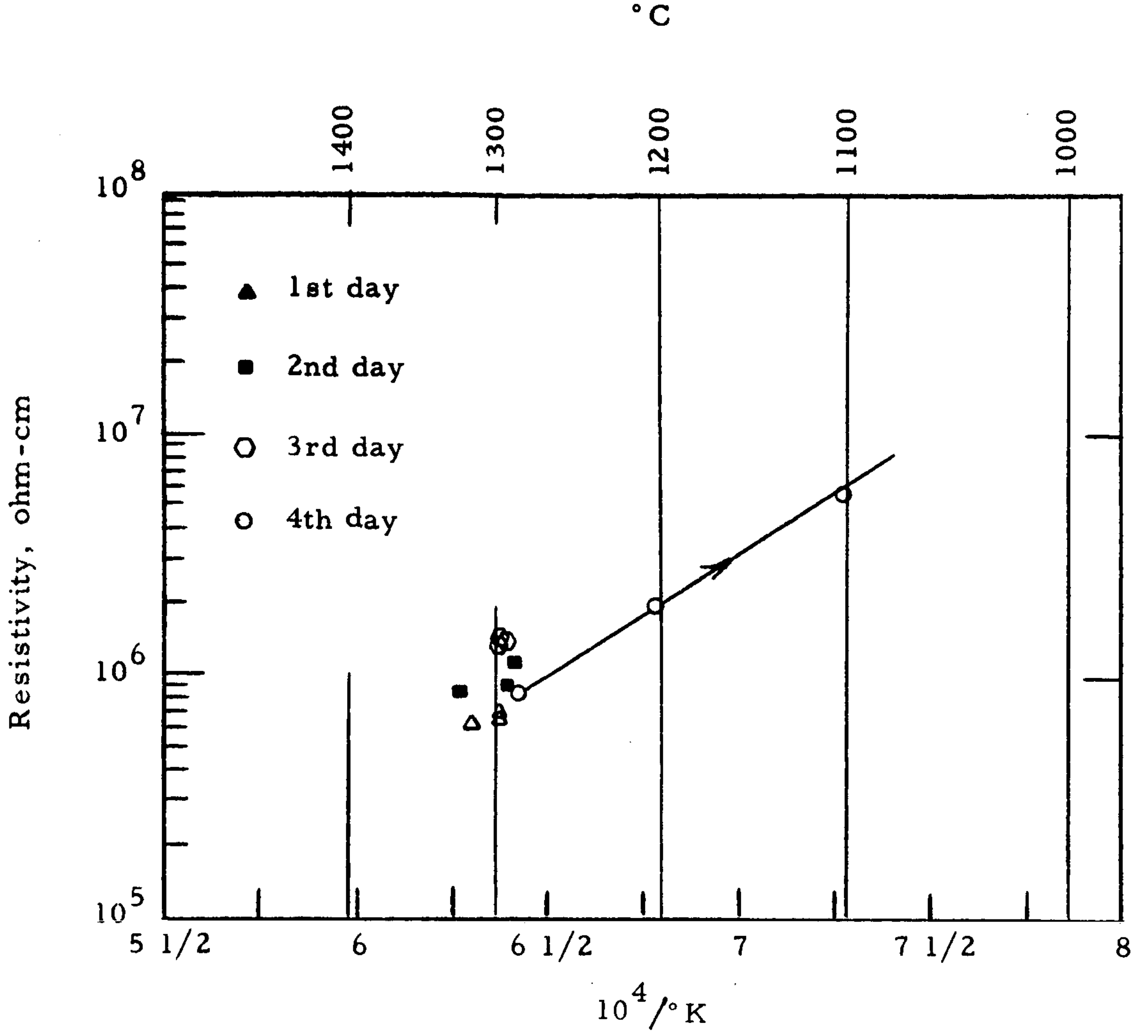


FIG. 9 - DC RESISTIVITY OF HIGH-PURITY ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN NITROGEN-2% HYDROGEN. Sample heated without an applied voltage. 1st and 2nd days, current measurements made from 0-90-0 volts, sample left on open circuit between measurements. 3rd and 4th days, current measuremnts made from 0-90-0 volts, sample left with 90 volts applied between measurements. Tungsten electrodes. Molybdenum susceptor.

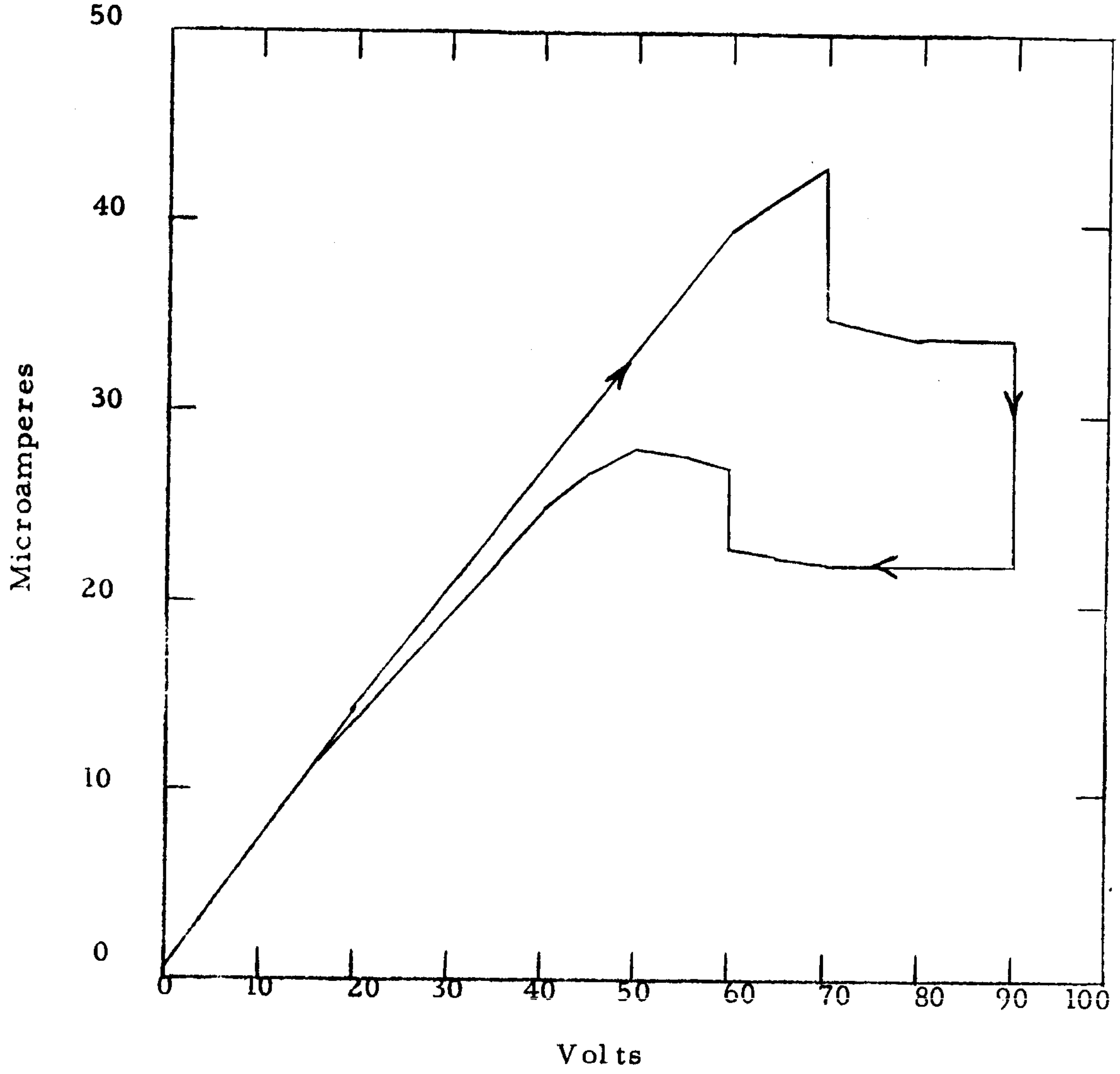


FIG. 10 - CURRENT VS. VOLTAGE FOR HIGH-PURITY ALUMINA (FIG. 9) AFTER 24 HOURS IN NITROGEN-2% HYDROGEN. Temperature 1290°C. Measurements made from 0-90-0 volts. Tungsten electrodes. Molybdenum susceptor.

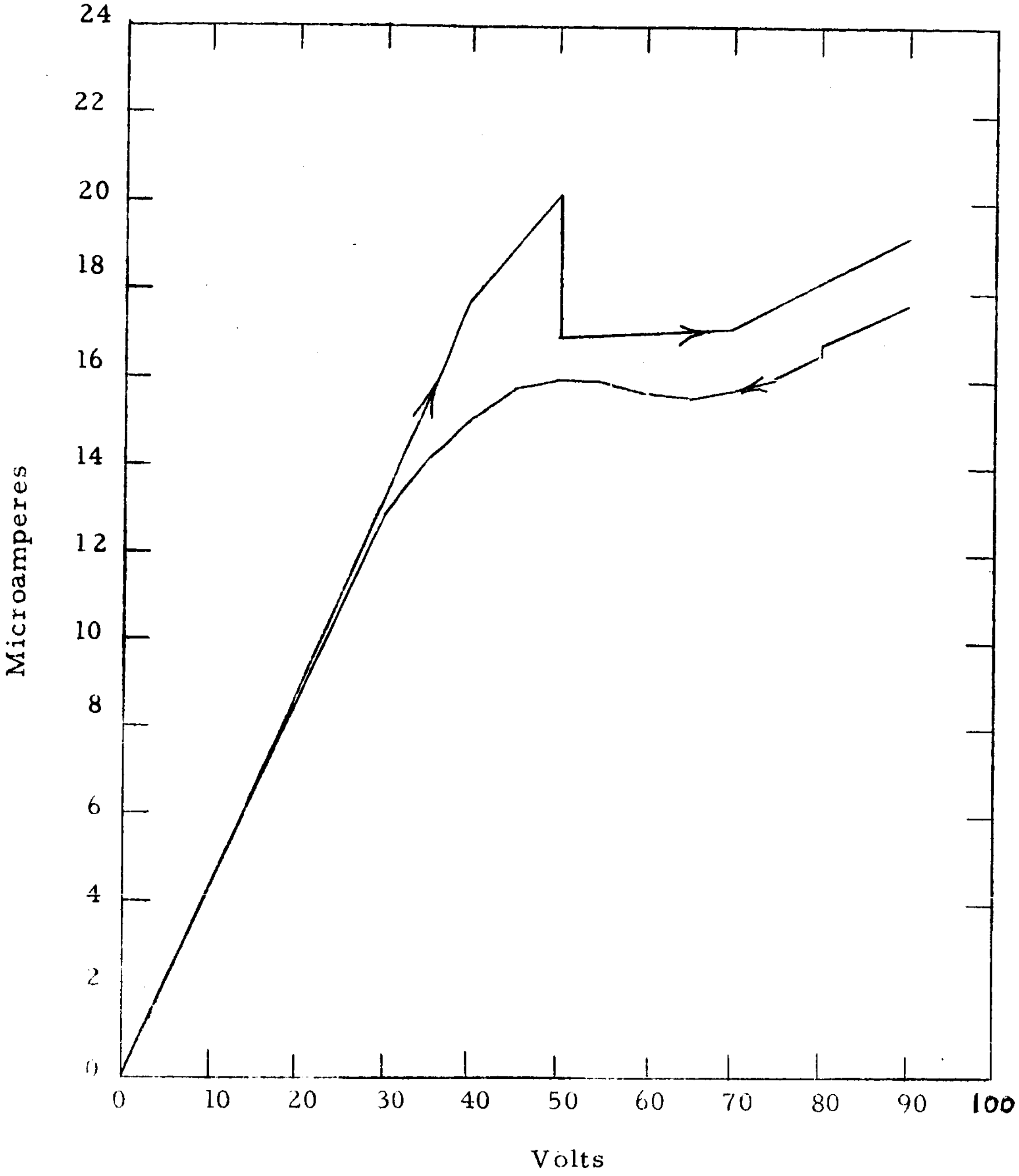


FIG. 11 - CURRENT VS. VOLTAGE FOR HIGH-PURITY ALUMINA (FIG. 9) AFTER 48 HOURS IN NITROGEN-2% HYDROGEN. Temperature 1290°C. Measurements made from 90-0-90 volts. Tungsten electrodes. Molybdenum susceptor.

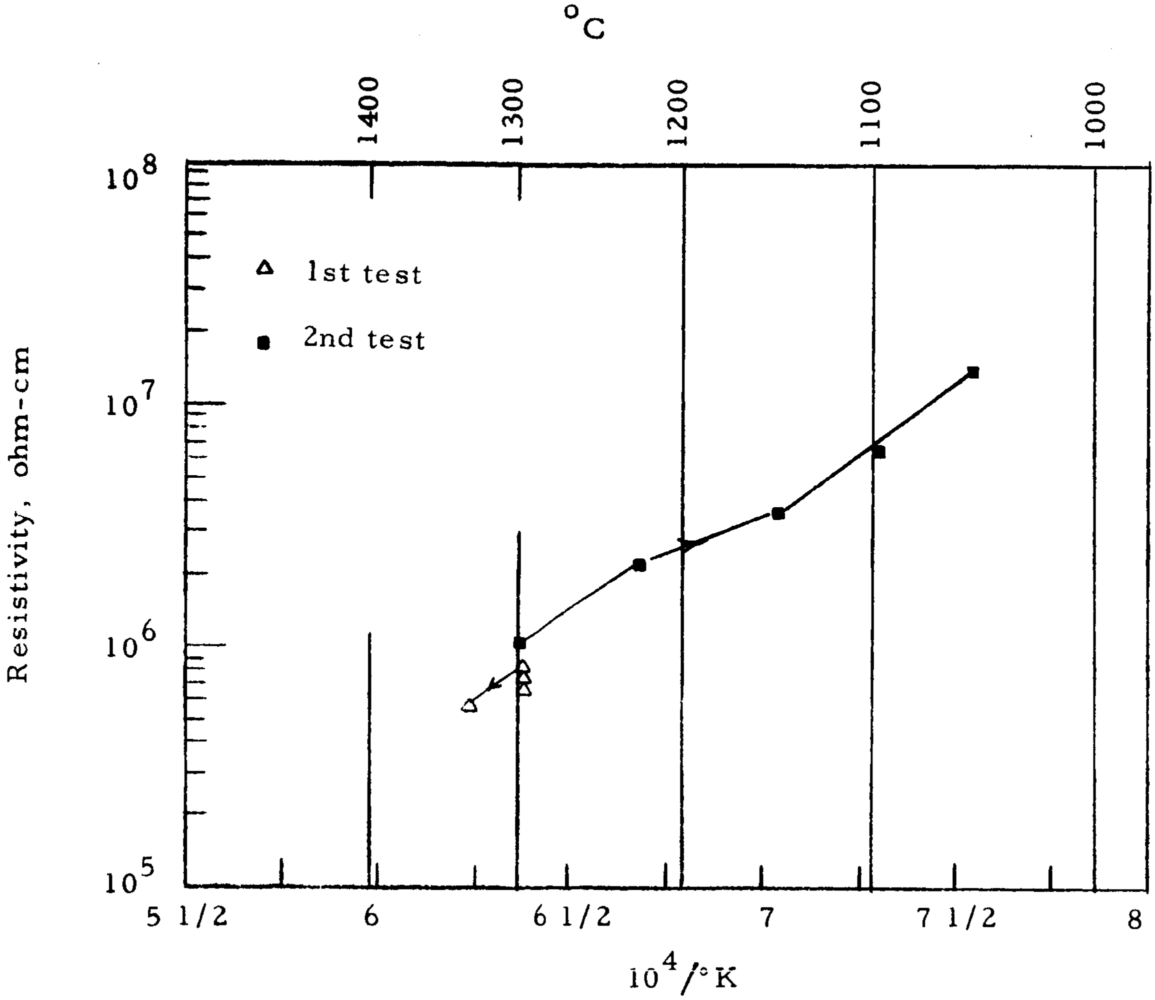


FIG. 12 - DC RESISTIVITY OF HIGH-PURITY ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN NITROGEN-2% HYDROGEN. Tungsten electrodes. Molybdenum susceptor.

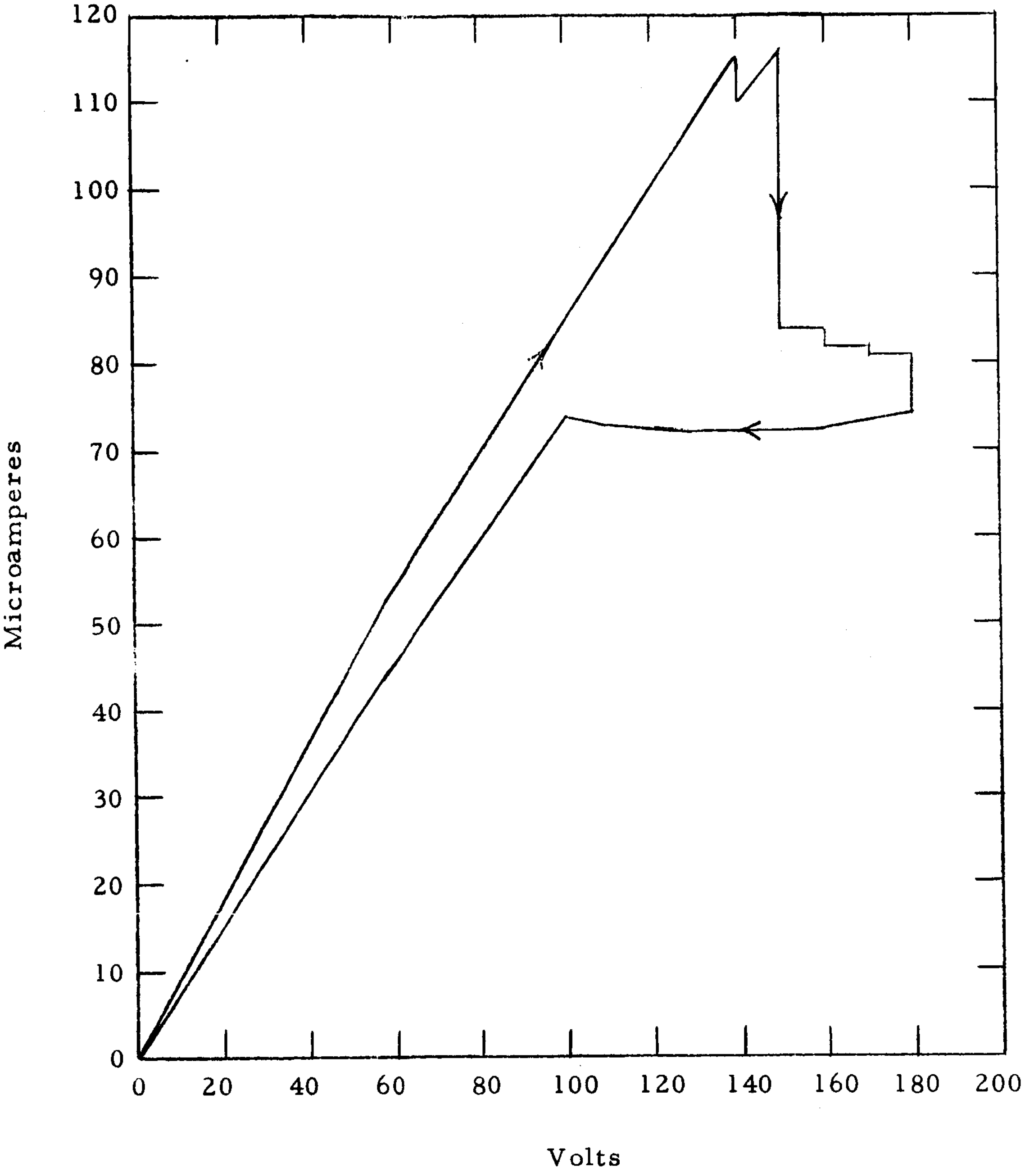


FIG. 13 - CURRENT VS. VOLTAGE FOR HIGH-PURITY ALUMINA (FIG. 12) AFTER 4 HOURS IN NITROGEN-2% HYDROGEN. Temperature 1290°C. Measurements made from 0-180-0 volts. Tungsten electrodes. Molybdenum susceptor.

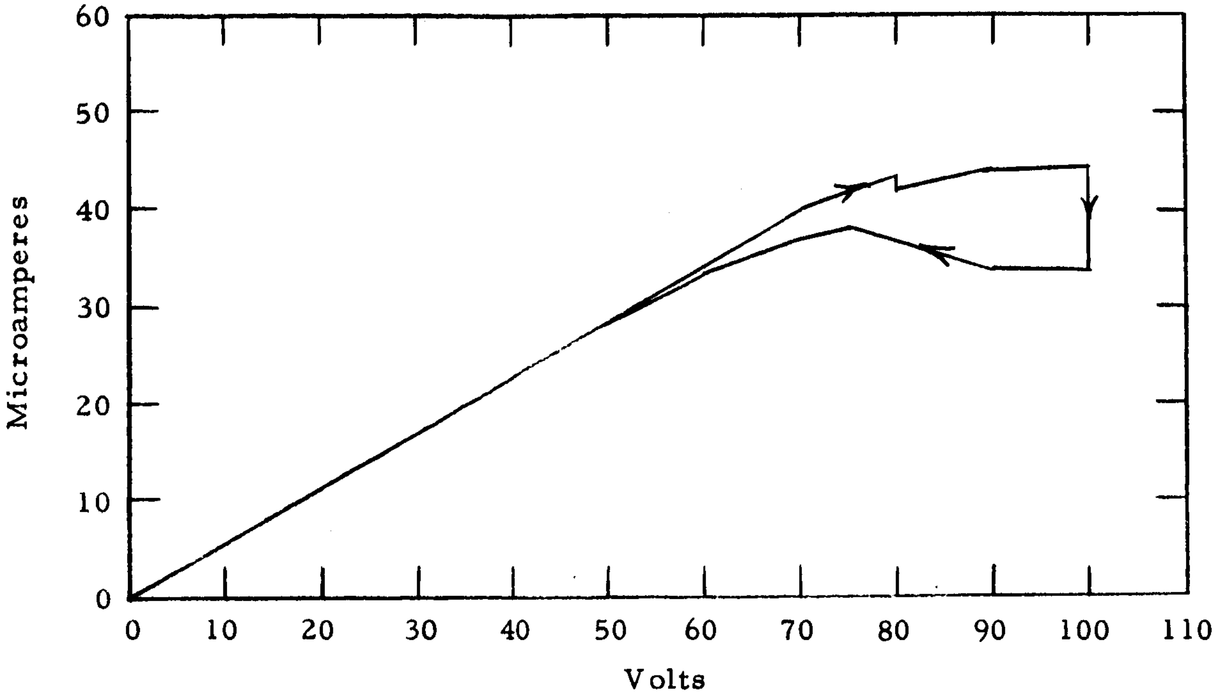


FIG. 14 - CURRENT VS. VOLTAGE FOR HIGH-PURITY ALUMINA (FIG. 12) AFTER 24 HOURS IN NITROGEN-2% HYDROGEN. Temperature 1295°C. Measurements made from 0-100-0 volts. Tungsten electrodes. Molybdenum susceptor.

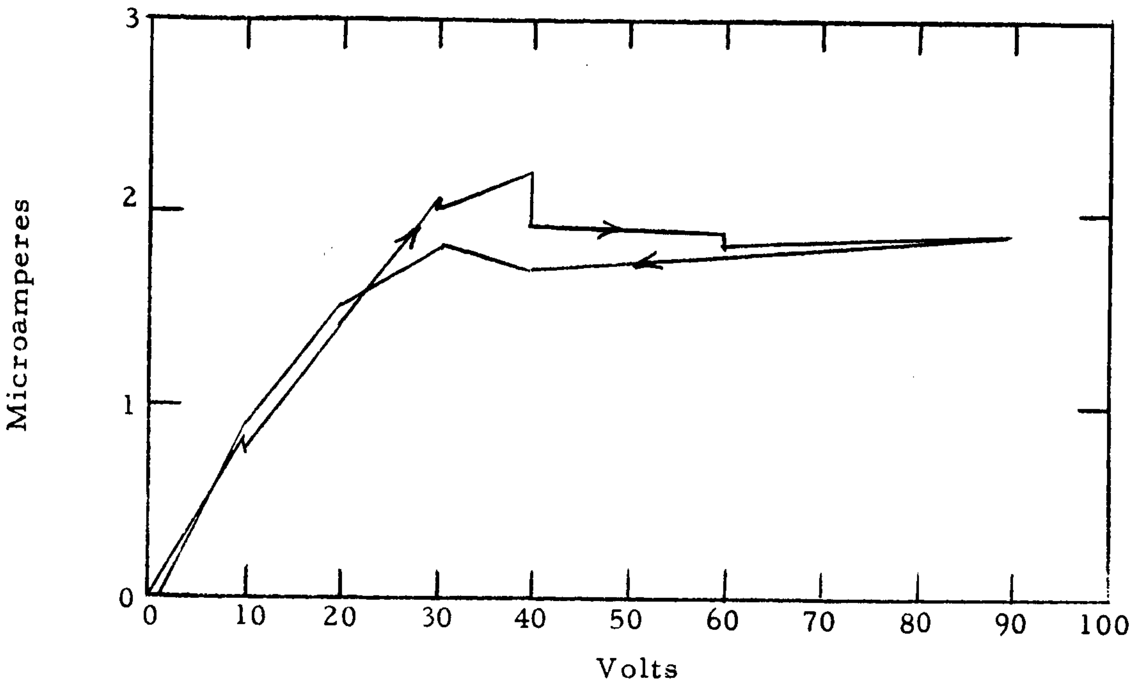


FIG. 15 - CURRENT VS. VOLTAGE FOR HIGH-PURITY ALUMINA (FIG. 12) AFTER 28 HOURS IN NITROGEN-2% HYDROGEN. Temperature 1095°C. Measurements made from 0-90-0 volts. Tungsten electrodes. Molybdenum susceptor.

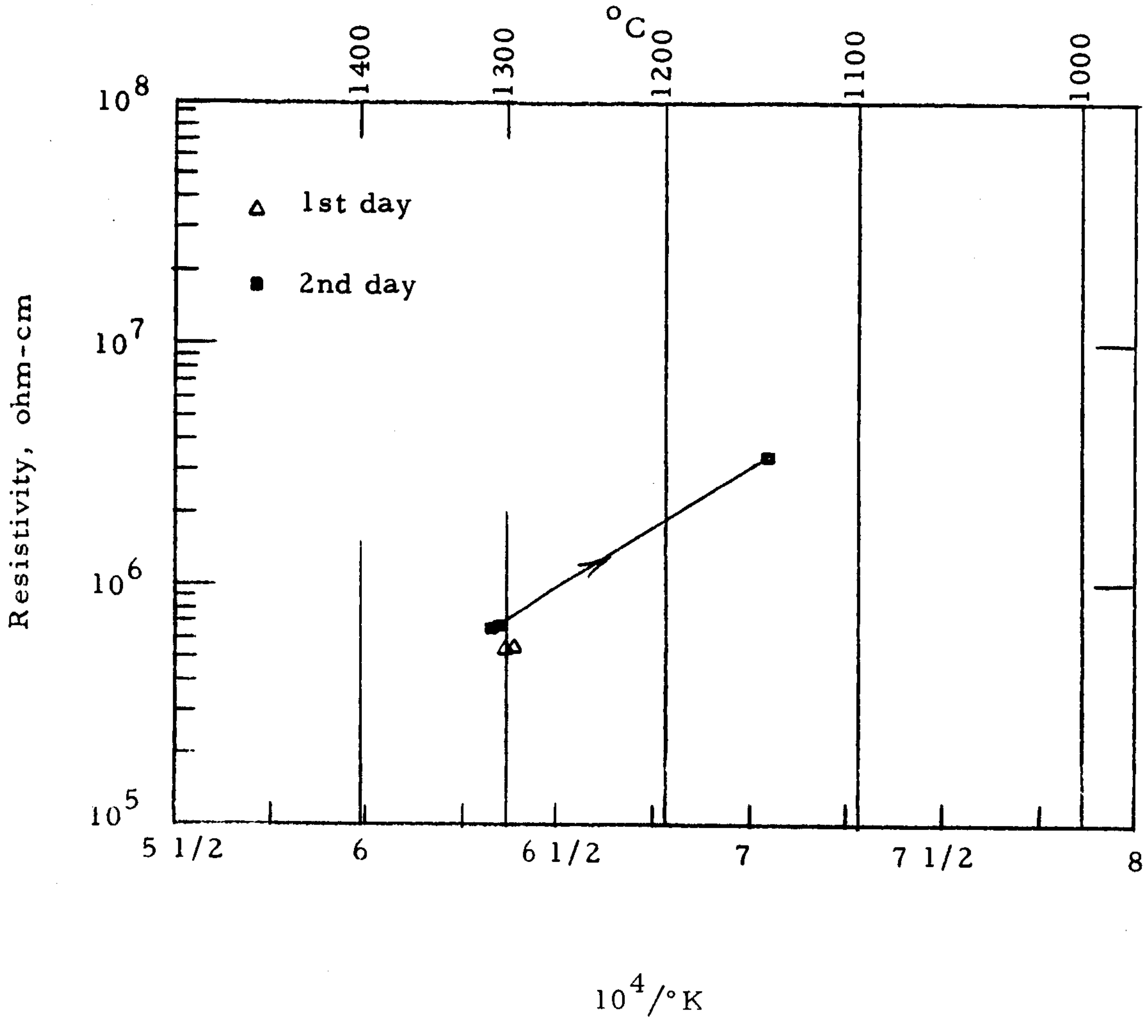


FIG. 16 - DC RESISTIVITY OF HIGH-PURITY ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN NITROGEN-2% HYDROGEN. Before test, sample was held at 1575°C for 1/2 hour in air and then quenched in air. Sample was heated in nitrogen without an applied voltage. Current measurements made from 0-maximum-0 volts. Sample was left without applied voltage between measurements. Tungsten electrodes. Molybdenum susceptor.

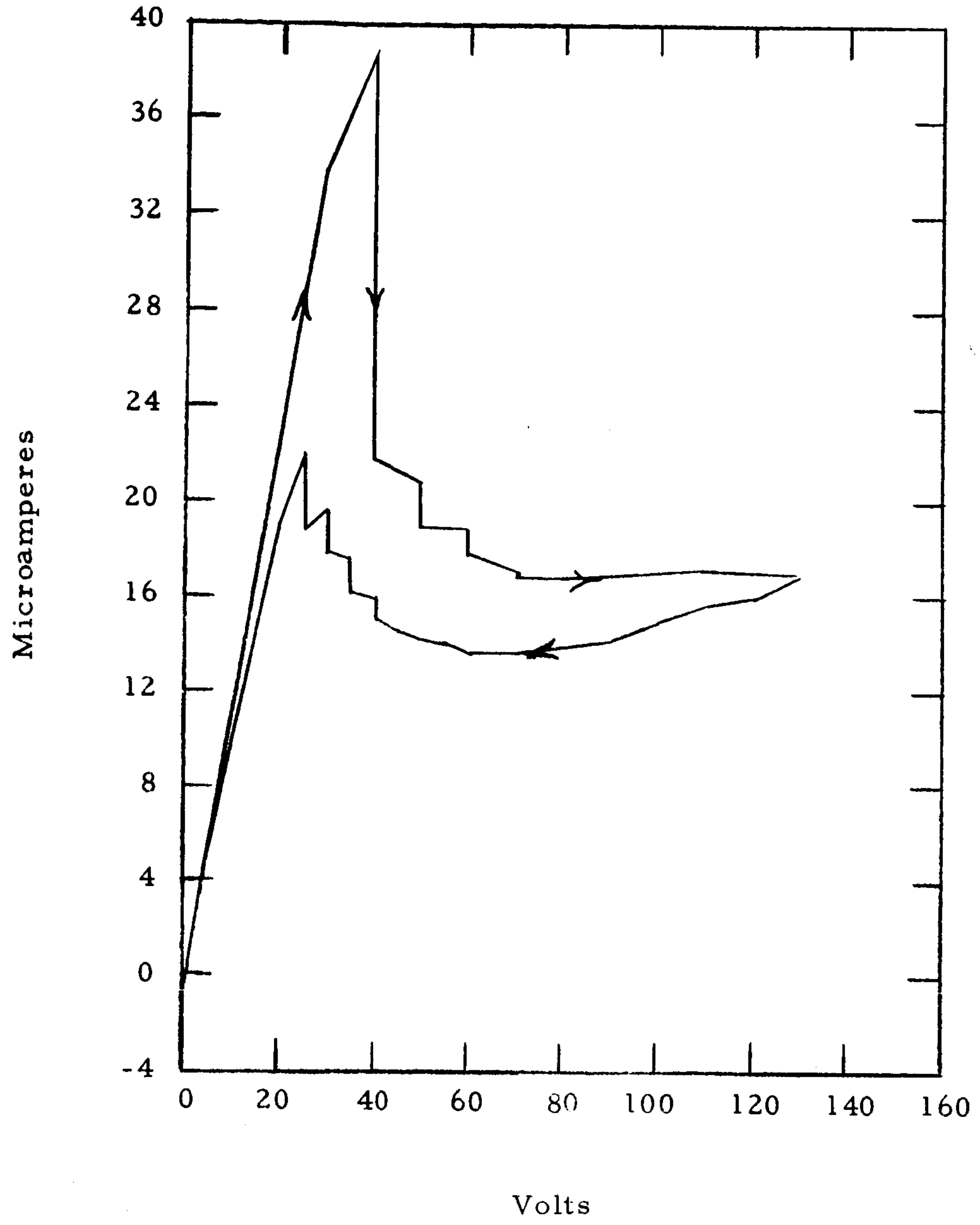


FIG. 17 - CURRENT VS. VOLTAGE FOR HIGH-PURITY ALUMINA (FIG. 16) AFTER 4 HOURS IN NITROGEN-2% HYDROGEN. Temperature 1295°C. Measurements made from 0-130-0 volts. Tungsten electrodes. Molybdenum susceptor.

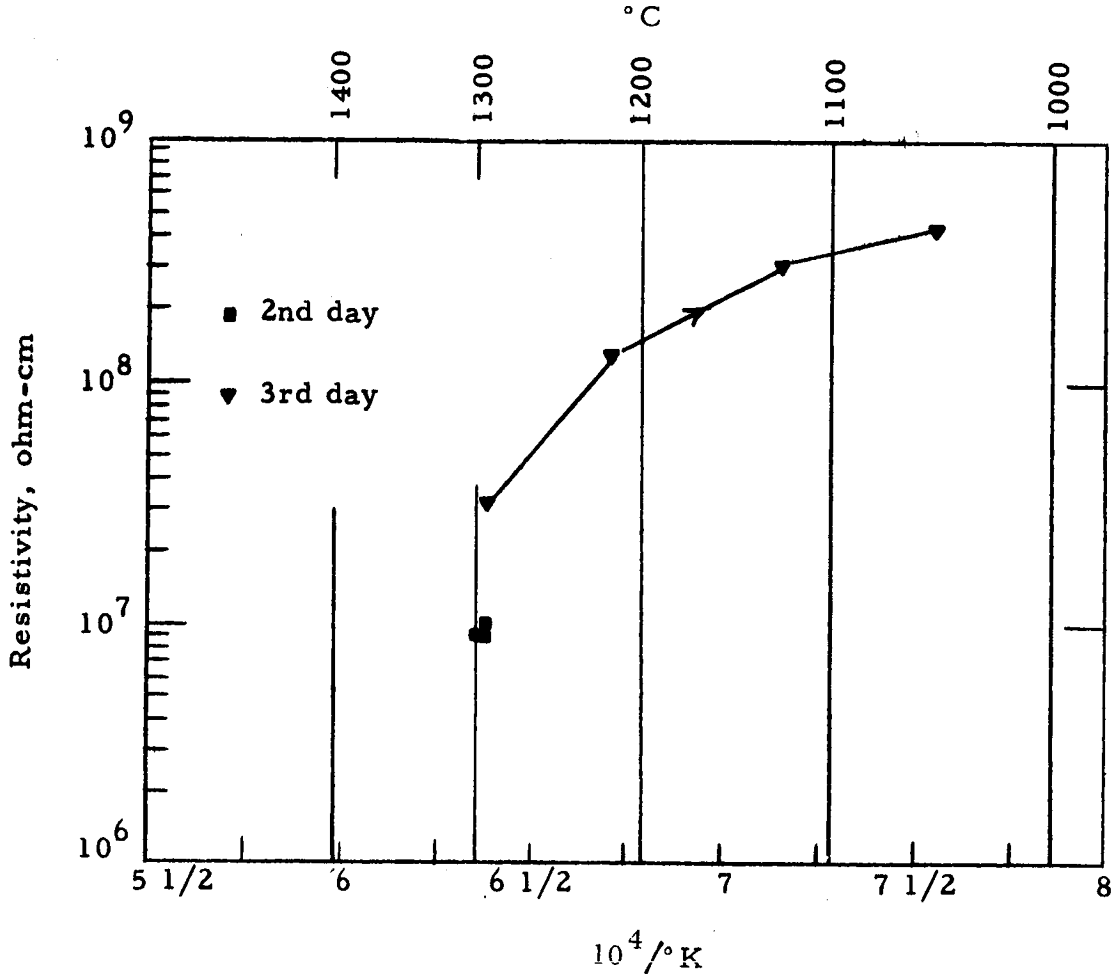


FIG. 18 - DC RESISTIVITY OF SAPPHIRE (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN NITROGEN-2% HYDROGEN. Sample heated without an applied voltage. Current measurements made from 0-180-0 volts. Sample was left without applied voltage between measurements. Tungsten electrodes. Molybdenum susceptor.

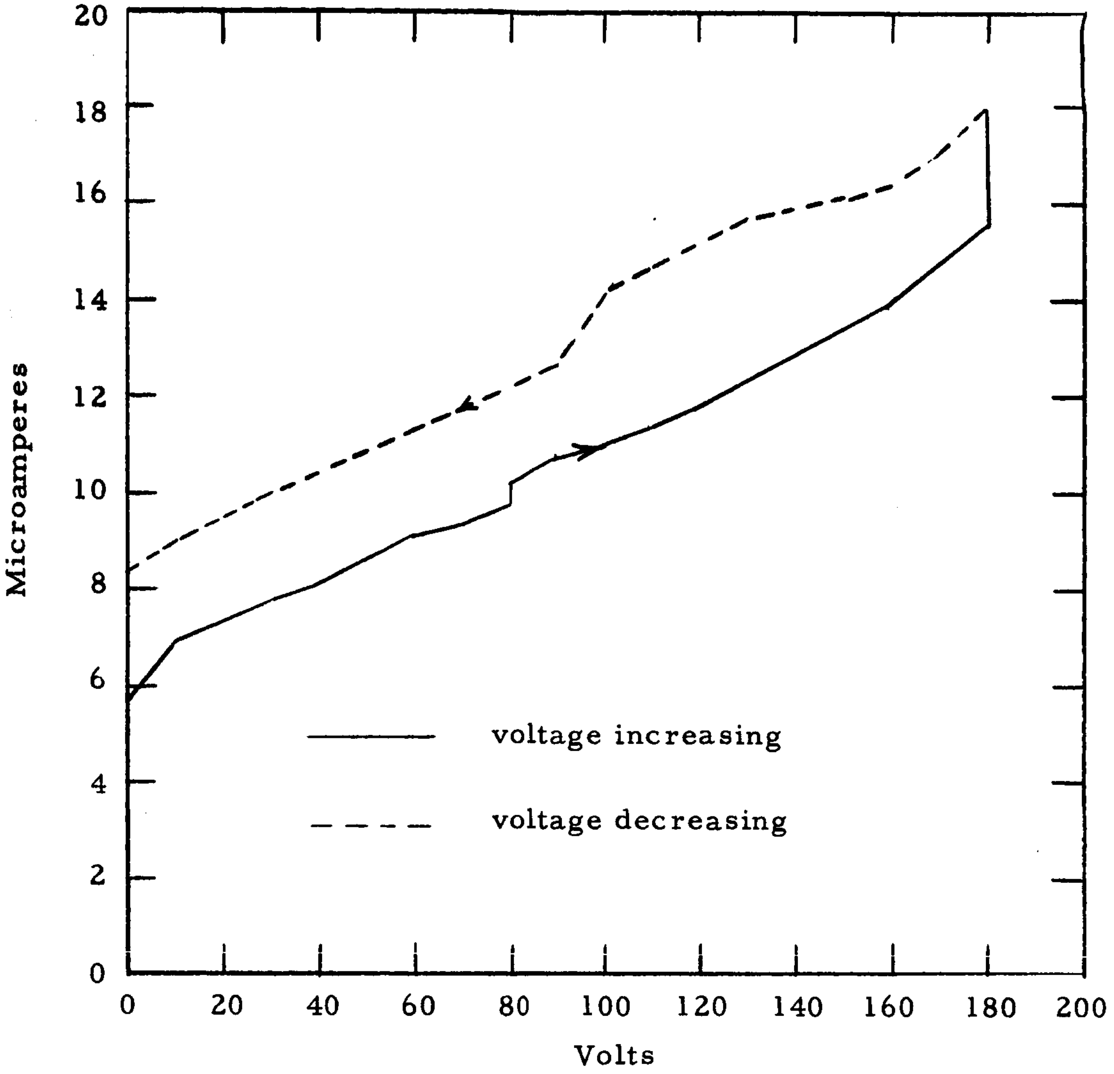


FIG. 19 - CURRENT VS. VOLTAGE FOR SAPPHIRE AFTER 4 HOURS IN NITROGEN-2% HYDROGEN. Temperature 1290°C. Measurements made from 0-180-0 volts. Tungsten electrodes. Molybdenum susceptor.

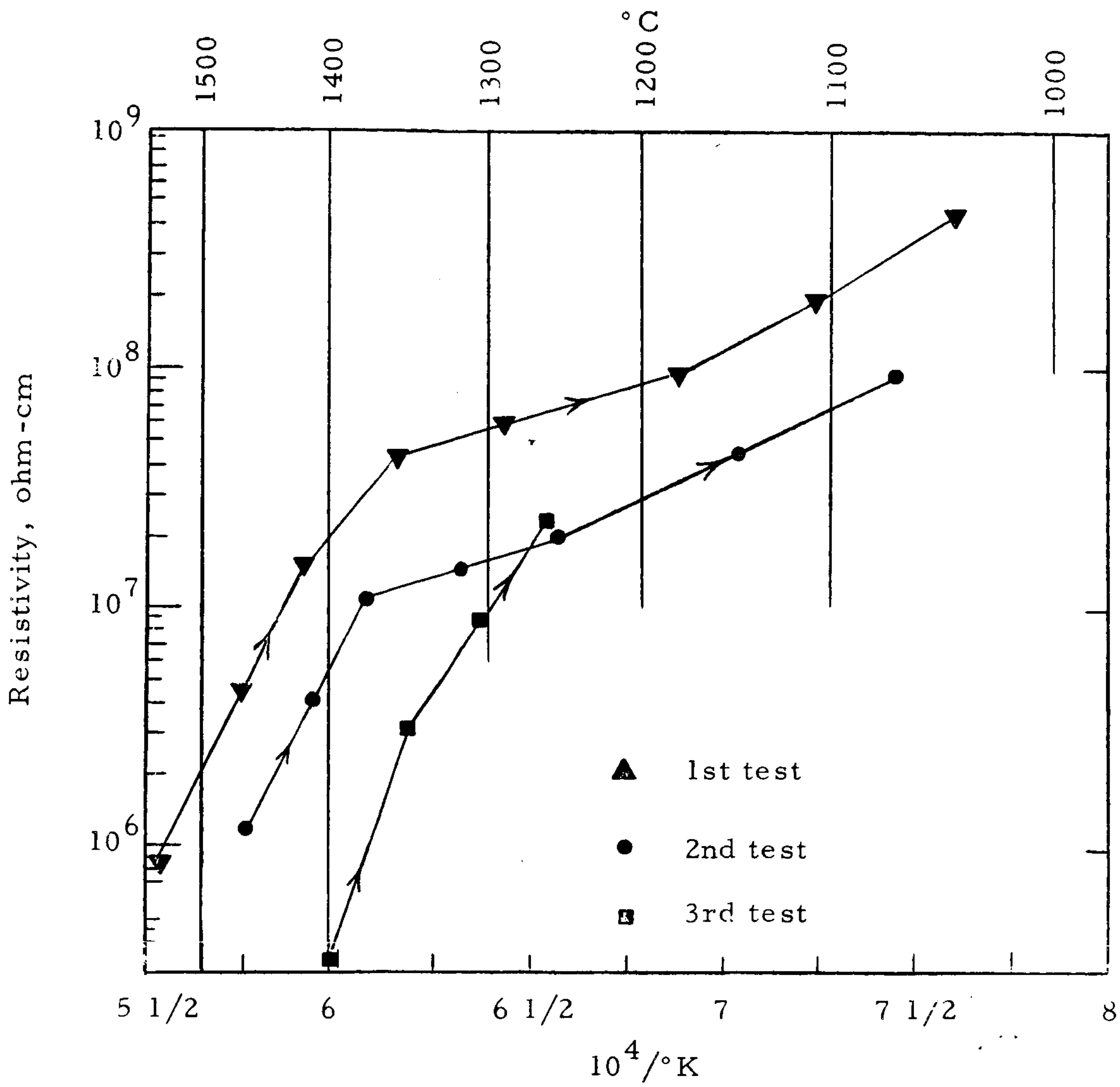


FIG. 20 - DC RESISTIVITY OF ALUCER ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN PREPURIFIED NITROGEN CONTAINING 500 PPM HYDROGEN--SUMMARY OF COOLING CYCLE CURVES. Tungsten electrodes at 90 V. Molybdenum susceptor. Sample previously tested using platinum susceptor.

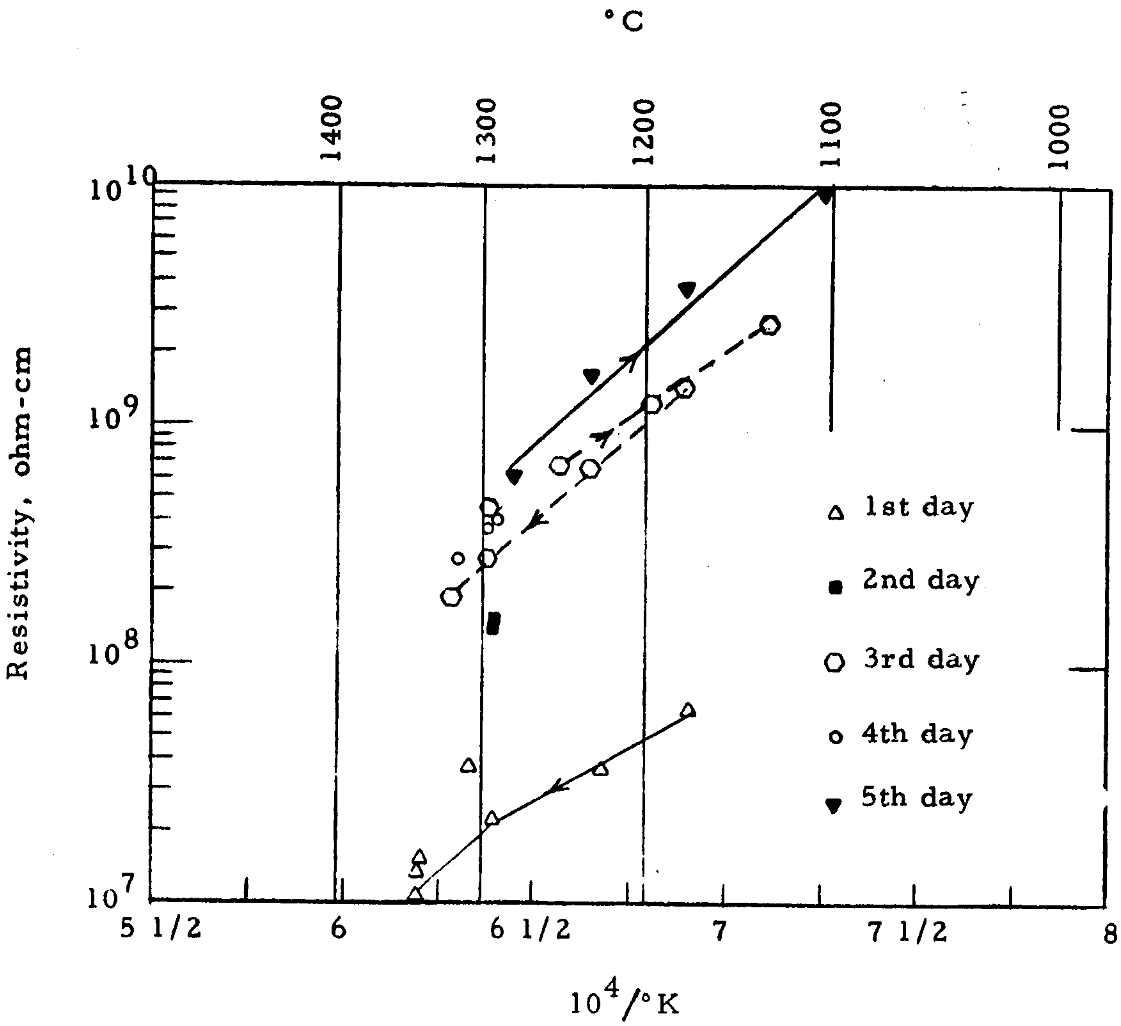


FIG. 21 - DC RESISTIVITY OF ALUCER ALUMINA (3/8 INCH DIAMETER BY 1/8 INCH THICK) IN NITROGEN CONTAINING 10% HYDROGEN. 100-hour test. Tungsten electrodes at 90 V. Platinum susceptor.

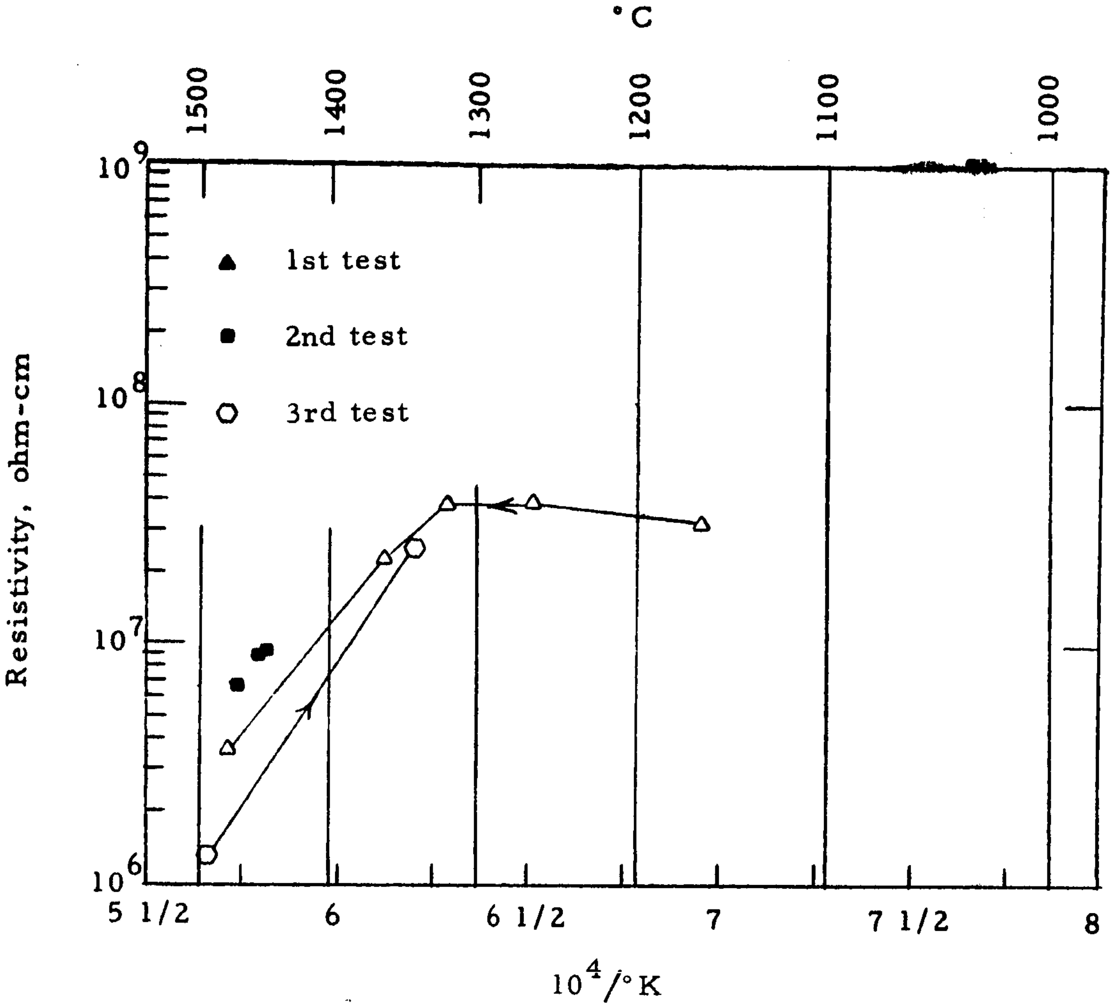


FIG. 22 - DC RESITIVITY OF ALUCER ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN NITROGEN CONTAINING 1%HYDROGEN. Tungsten electrodes at 90 V. Platinum susceptor.

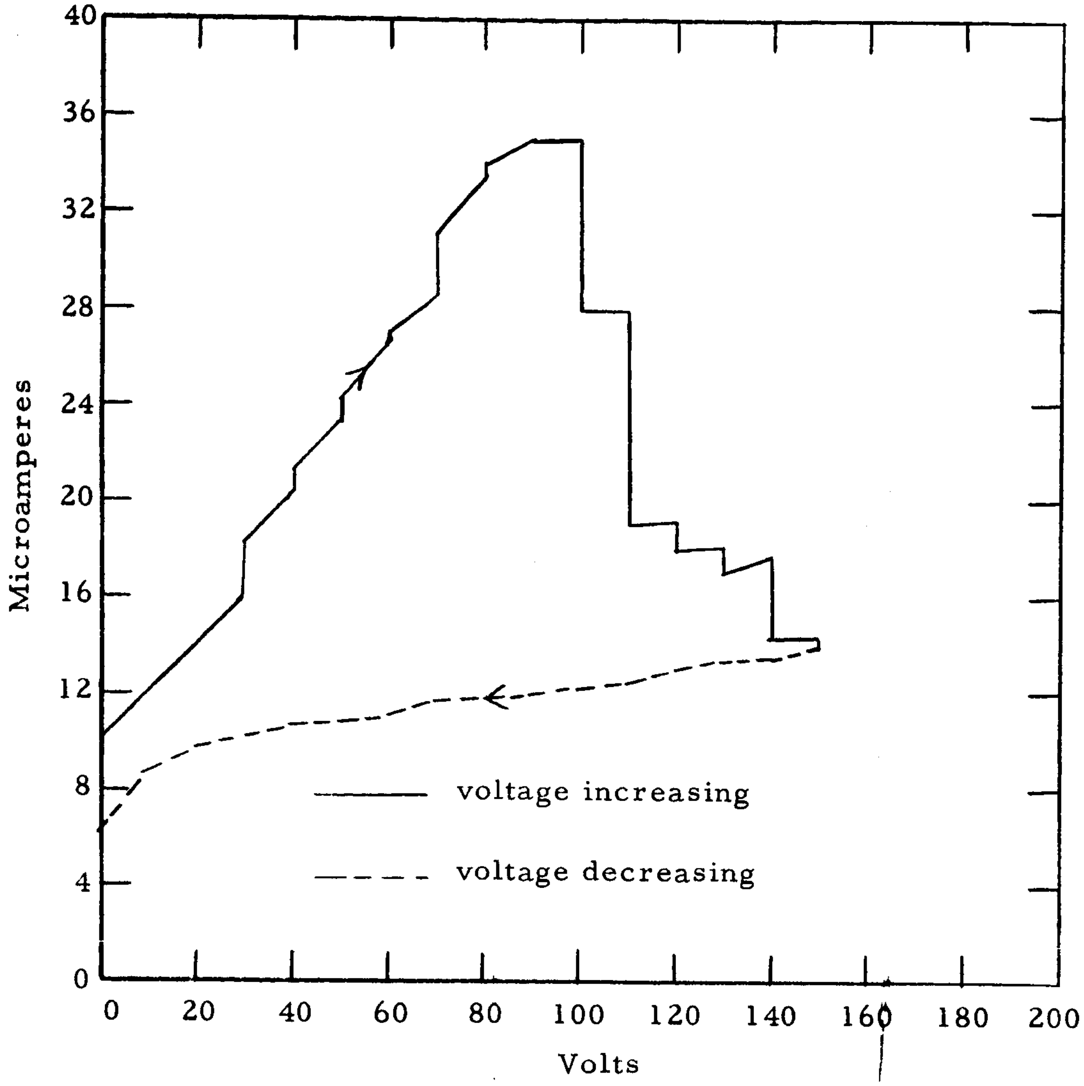


FIG. 23 - CURRENT VS. VOLTAGE FOR ALUCER ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) AFTER 4 HOURS IN NITROGEN-2% HYDROGEN. Temperature 1275°C. Measurements made from 0-150-0 volts. Tungsten electrodes. Molydenum susceptor.

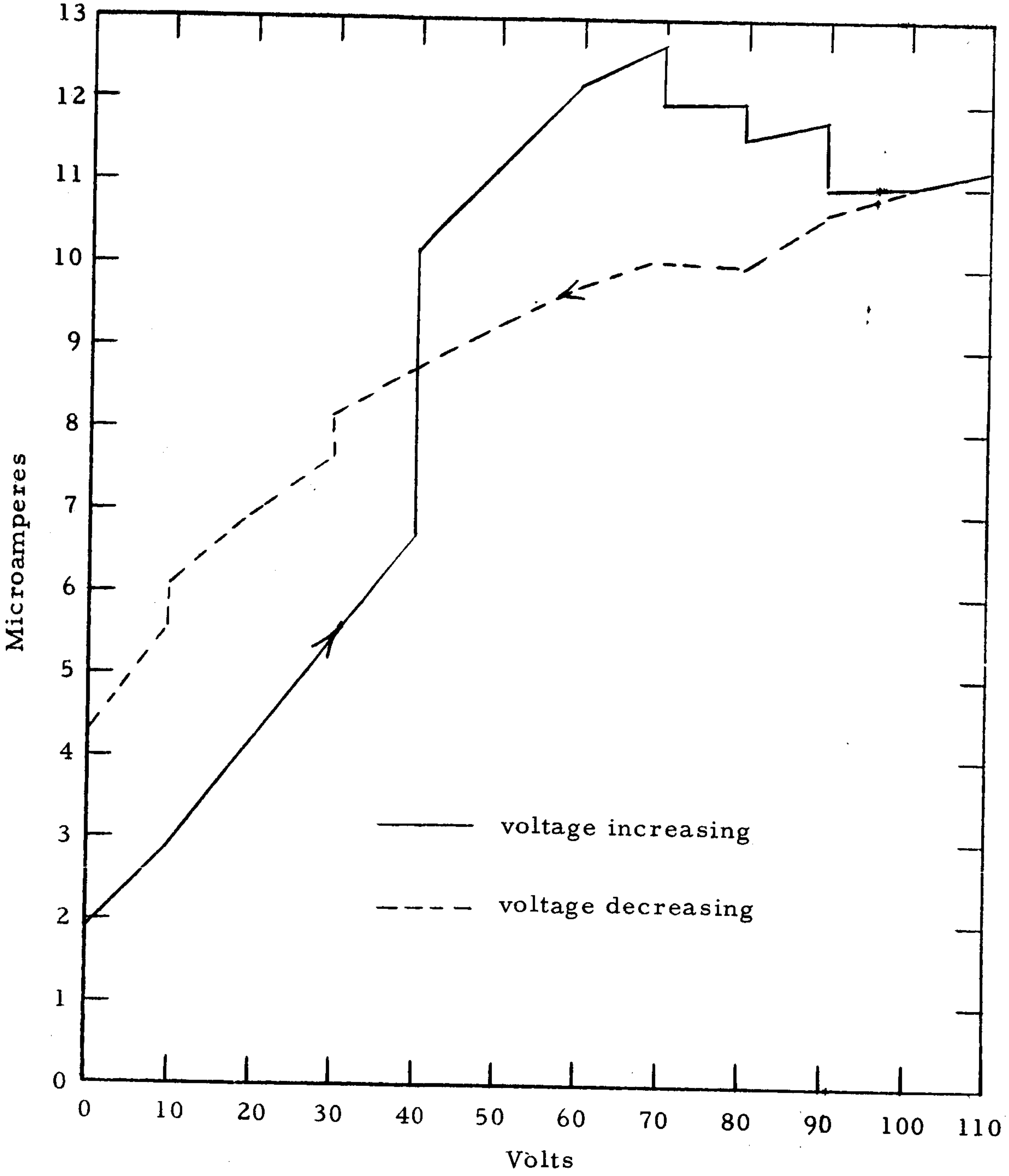


FIG. 24 - CURRENT VS. VOLTAGE FOR ALUCER ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) AFTER 27 HOURS IN NITROGEN-2% HYDROGEN. Temperature 1300°C. Measurements made from 0-110-0 volts. Tungsten electrodes. Molybdenum susceptor.

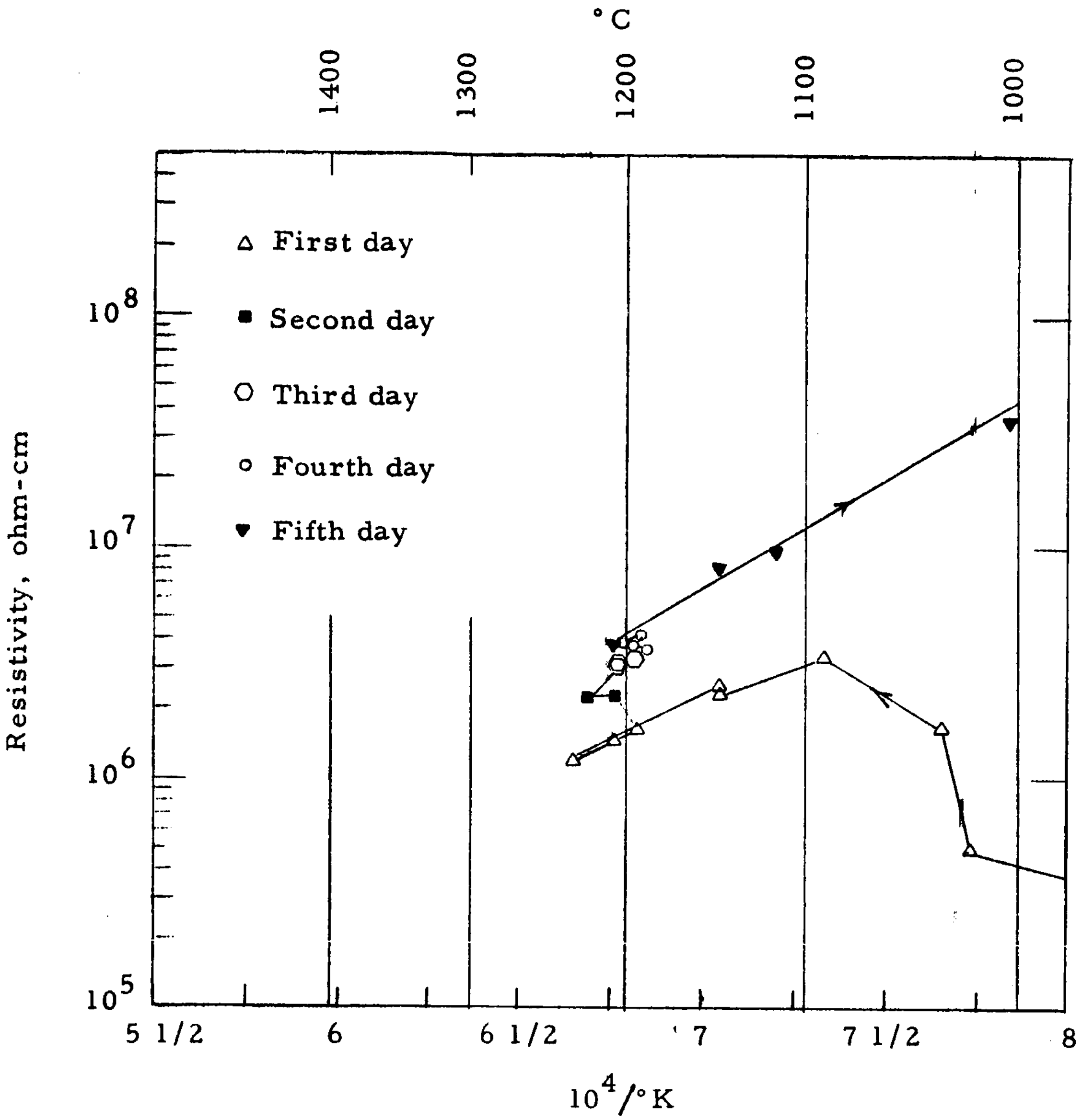


FIG. 25 - DC RESISTIVITY OF HIGH-PURITY ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN HYDROGEN-ARGON. 100-hour test. Tungsten electrodes at 90 V. Platinum susceptor.

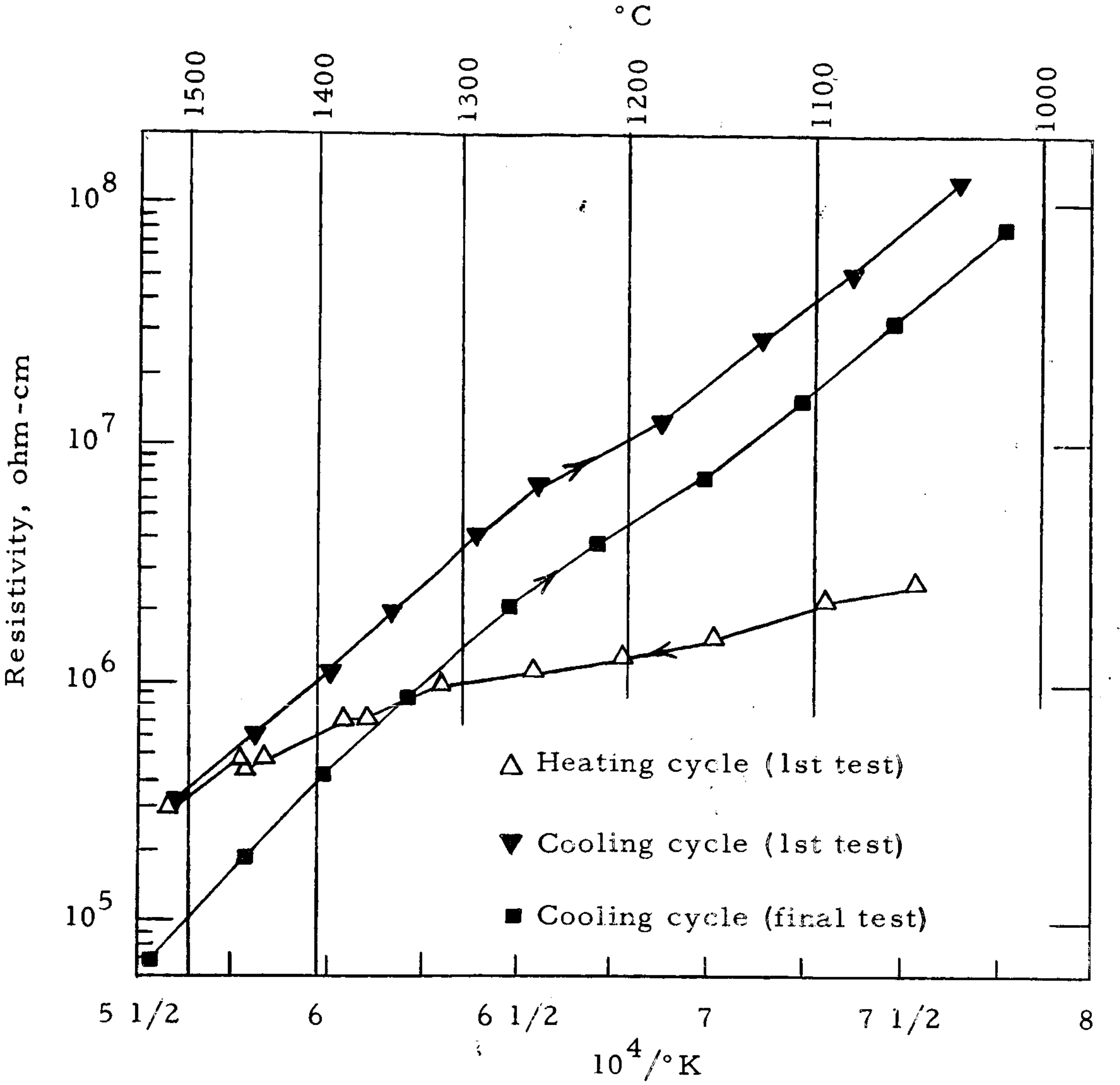


FIG. 26 - DC RESISTIVITY OF HIGH-PURITY ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN HYDROGEN-ARGON--HEATING AND COOLING CYCLE CURVES FOR FIRST AND FINAL TESTS ARE SHOWN. Tungsten electrodes at 90 V. Graphite susceptor.

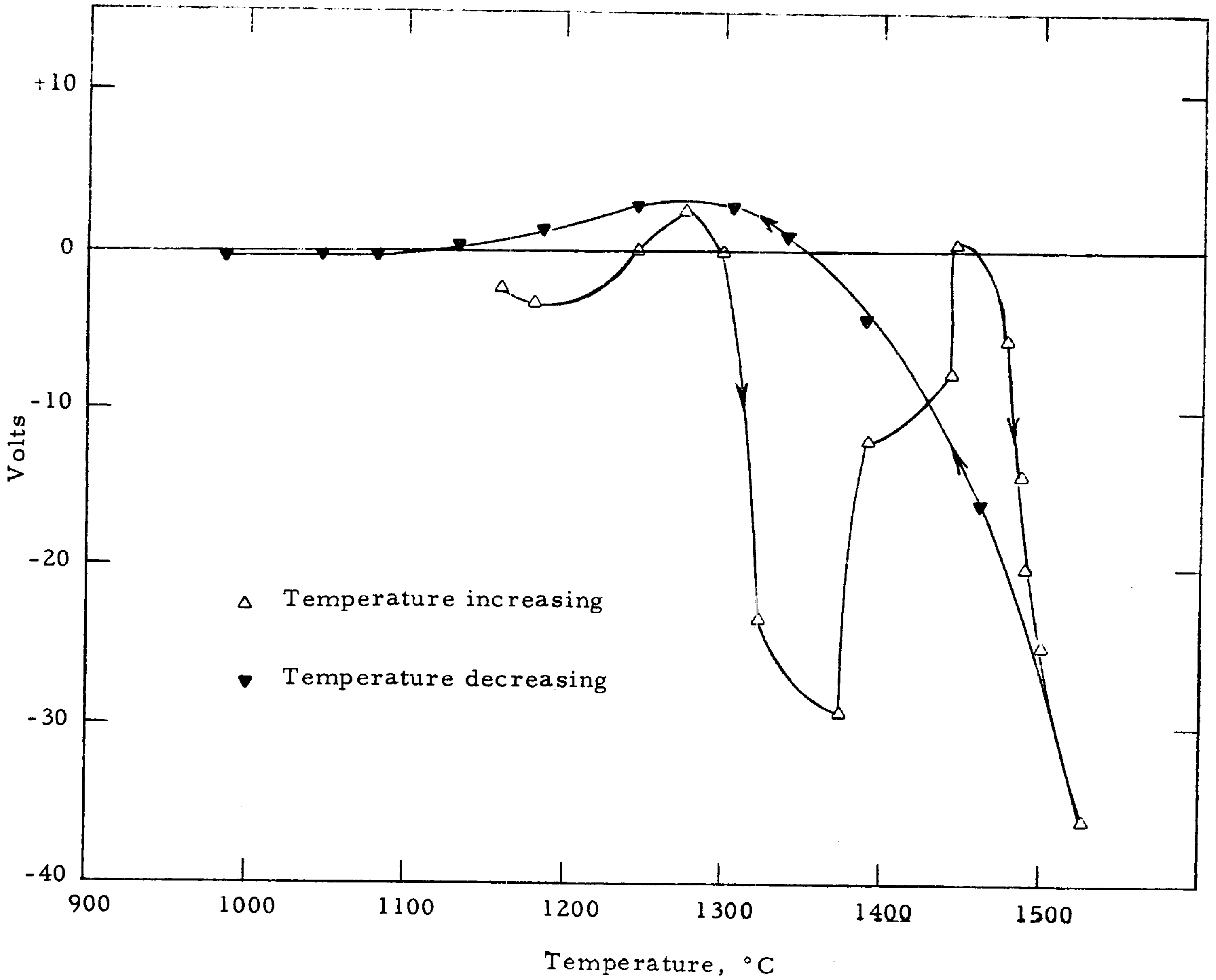


FIG. 27 - OPEN-CIRCUIT EMF DEVELOPED BY HIGH-PURITY ALUMINA IN HYDROGEN-ARGON. Tungsten electrodes. Graphite susceptor. Sample previously tested with 90 VDC applied.

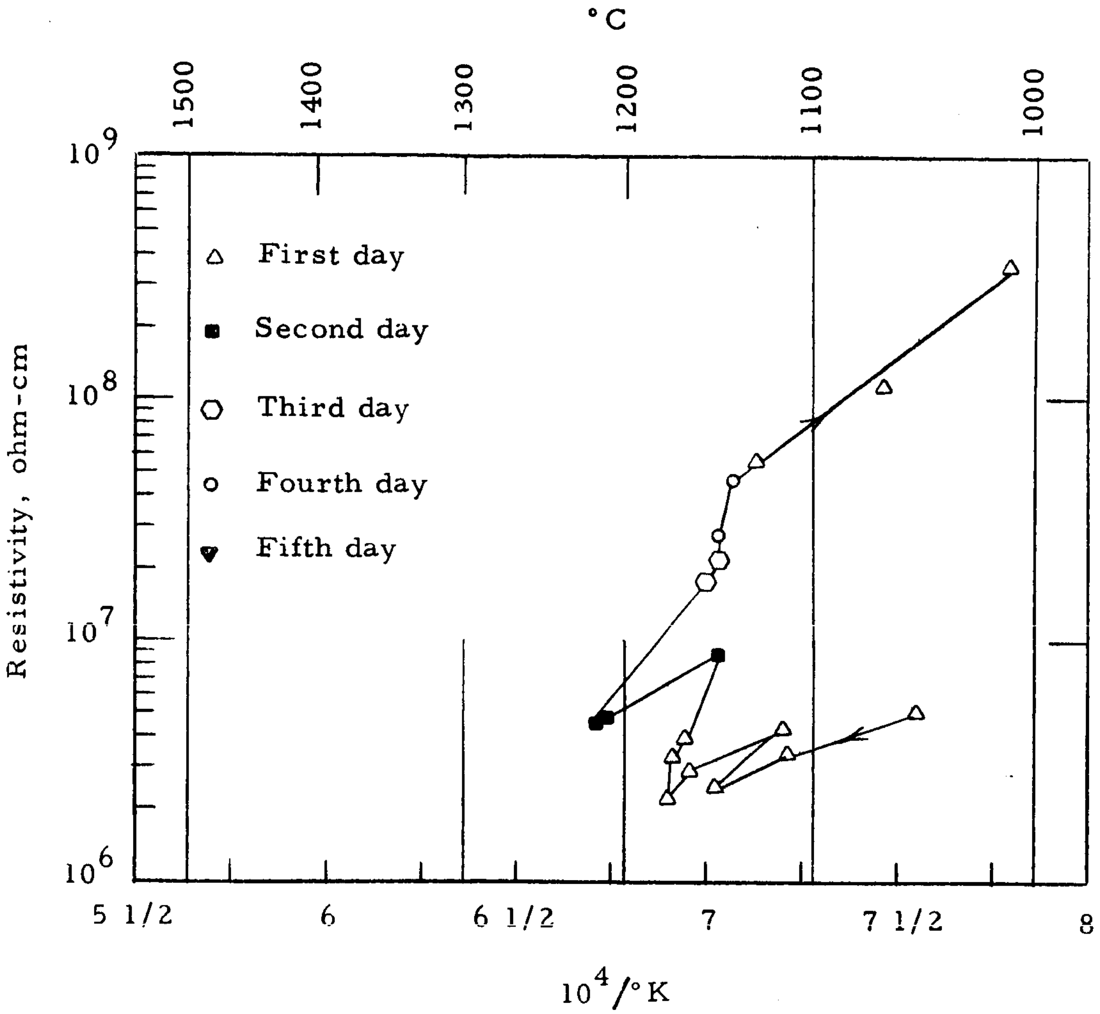


FIG. 28 - DC RESISTIVITY OF HIGH-PURITY ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN HYDROGEN-ARGON. 100-hour test. Tungsten electrodes at 90 V. Tantalum susceptor.

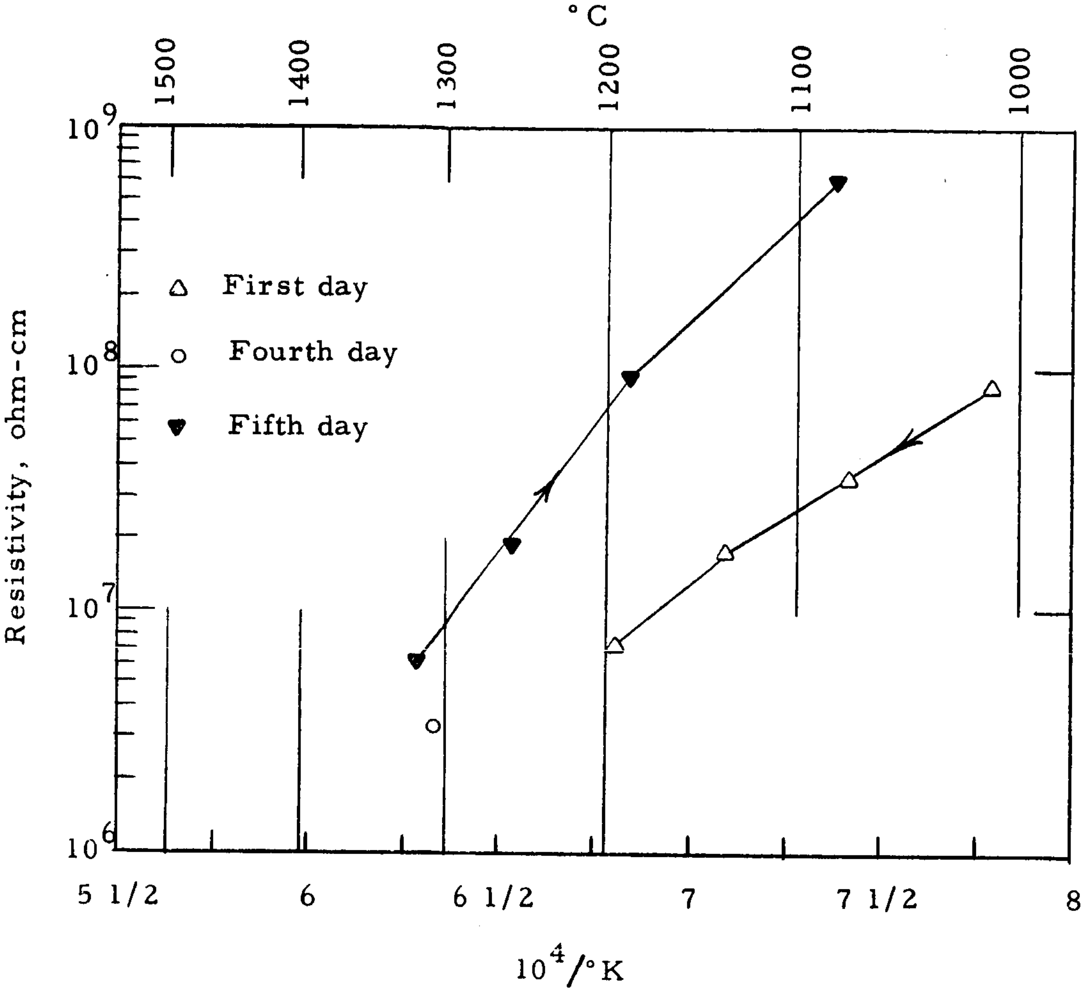


FIG. 29 - DC RESISTIVITY OF HIGH-PURITY ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN HYDROGEN-ARGON. 100-hour test. Tungsten electrodes at 90 V. Molybdenum susceptor. Sample previously tested for 100 hours with tantalum susceptor.

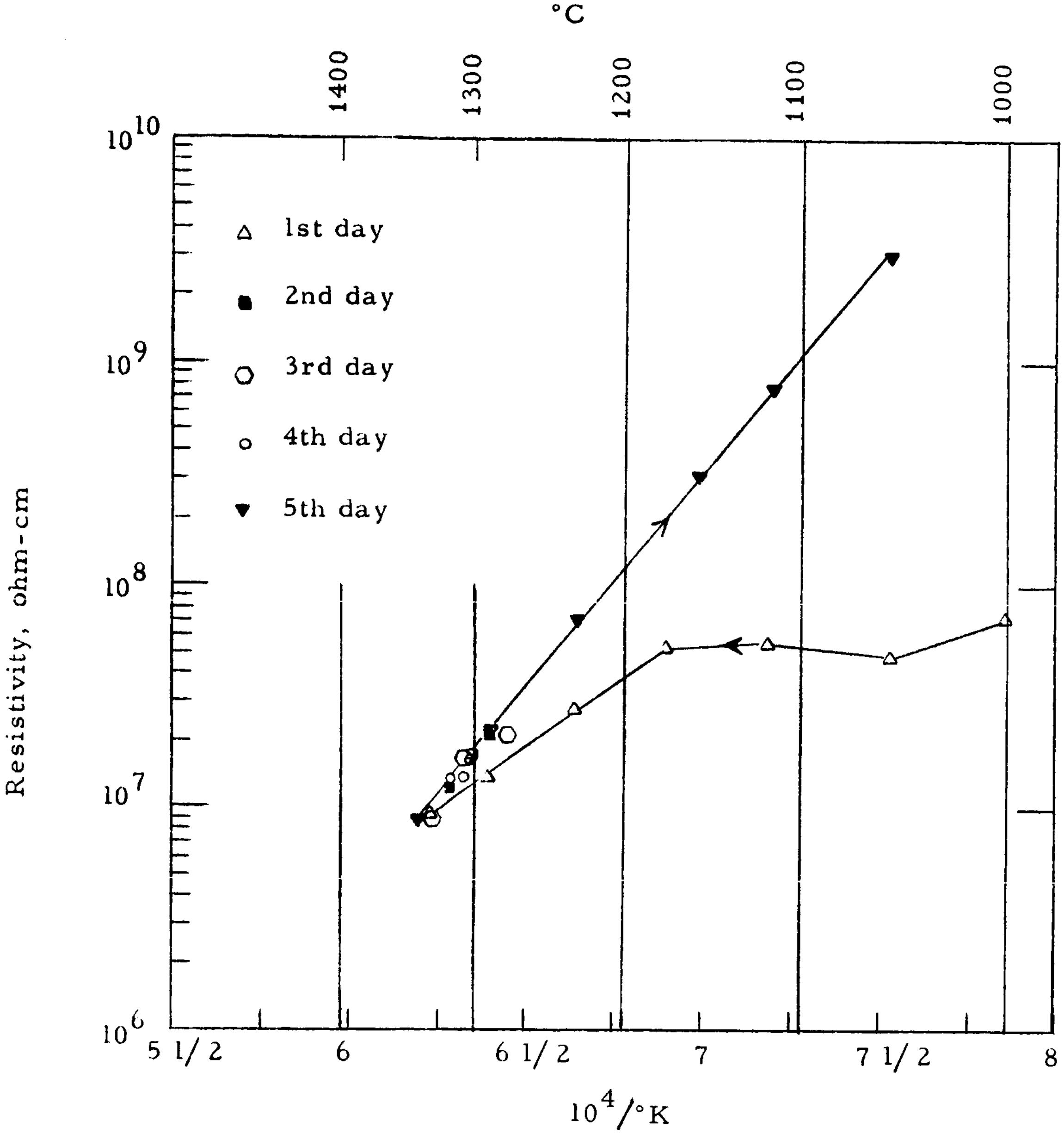


FIG. 30 - DC RESISTIVITY OF SAPPHIRE (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN HYDROGEN-ARGON. 100-hour test. Tungsten electrodes at 90 V. Molybdenum susceptor.

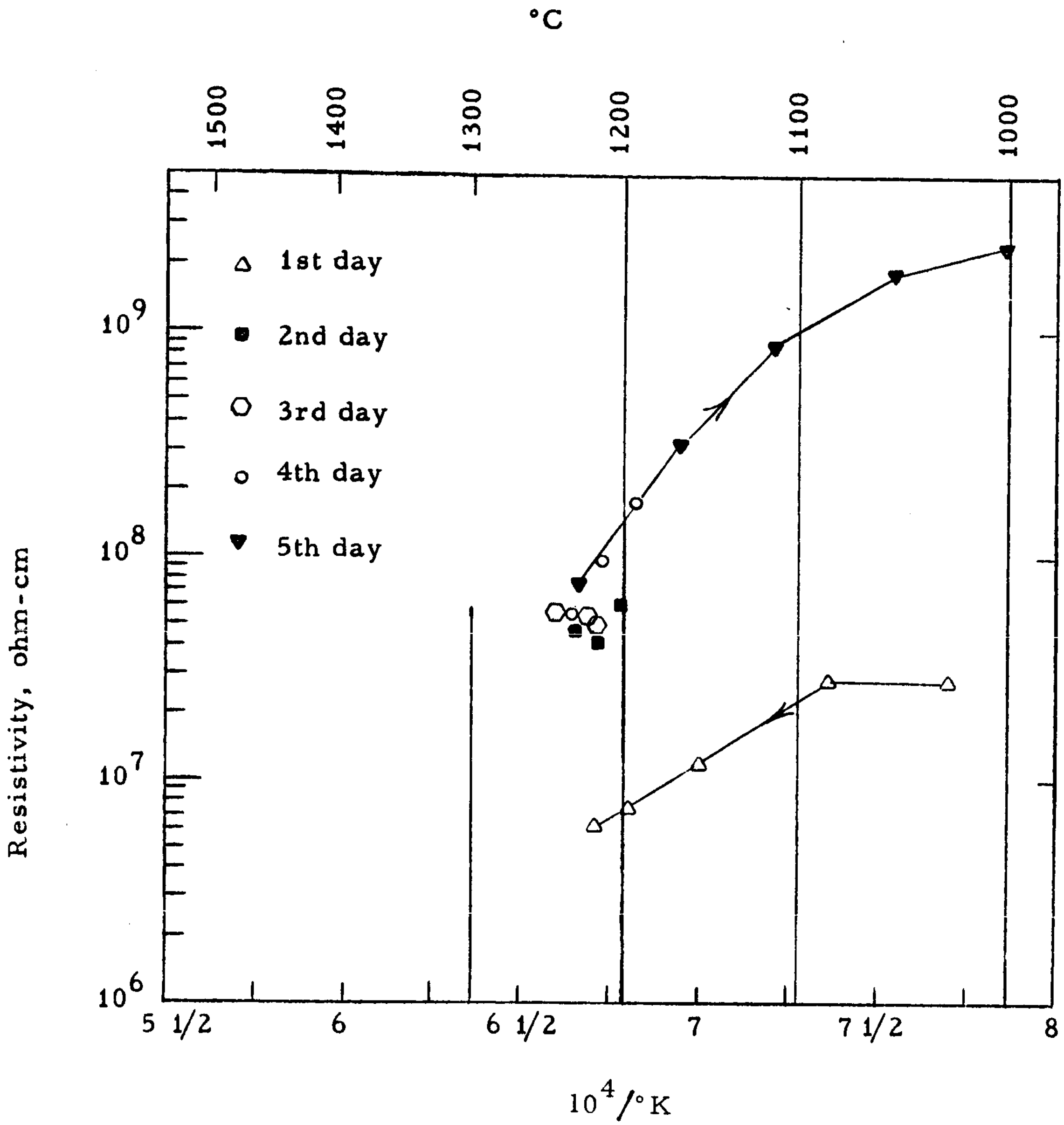


FIG. 31 - DC RESISTIVITY OF ALUCER ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN HYDROGEN-ARGON. 100-hour test. Tungsten electrodes at 90 V. Molybdenum susceptor.

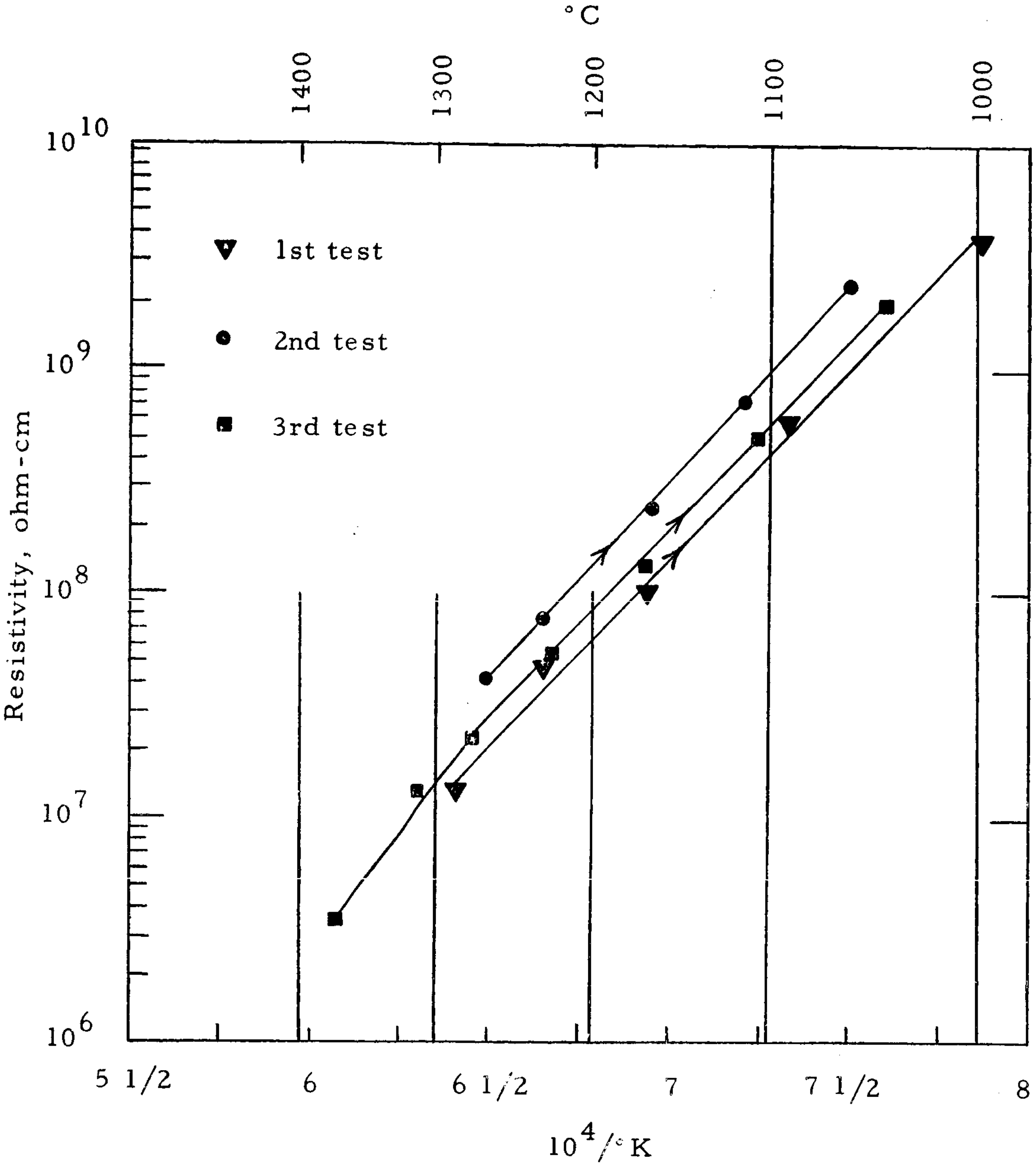


FIG. 32 - DC RESISTIVITY OF ALUCER ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN HYDROGEN-ARGON--SUMMARY OF COOLING CYCLE CURVES. Tungsten electrodes at 90 V. Molybdenum susceptor.

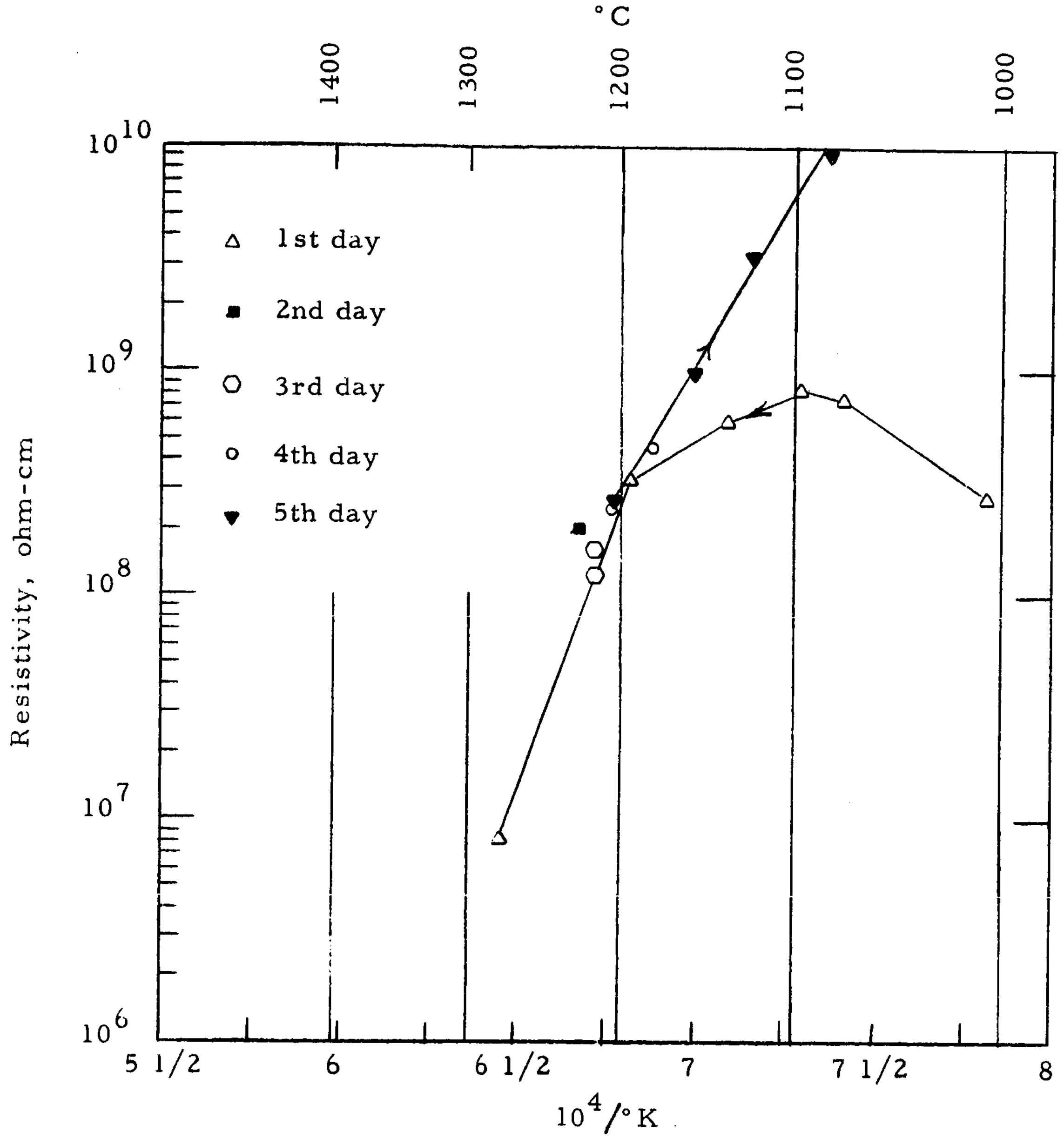


FIG. 33 - DC RESISTIVITY OF ALUCER ALUMINA (3/8 INCH DIAMETER BY 1/8 INCH THICK) IN HYDROGEN-ARGON. 100-hour test. Tungsten electrodes at 90 V. Molybdenum susceptor.

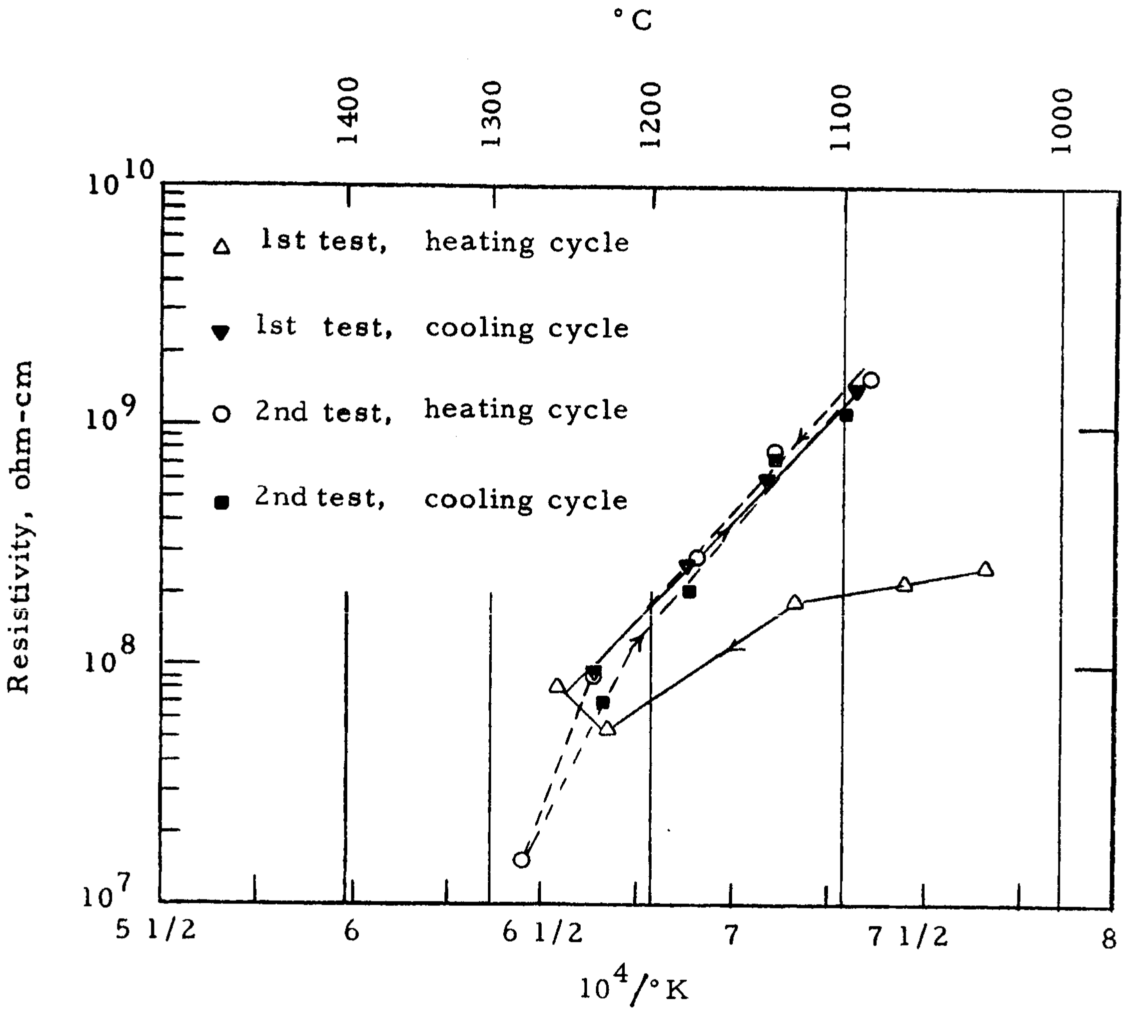


FIG. 34 - DC RESISTIVITY OF ALUCER ALUMINA (3/8 INCH DIAMETER BY 1/8 INCH THICK) IN MERCURY VAPOR WITH HYDROGEN-ARGON CARRIER--TWO TESTS. Mercury at 110° and 114°C. Tungsten electrodes at 90 V. Molybdenum susceptor.

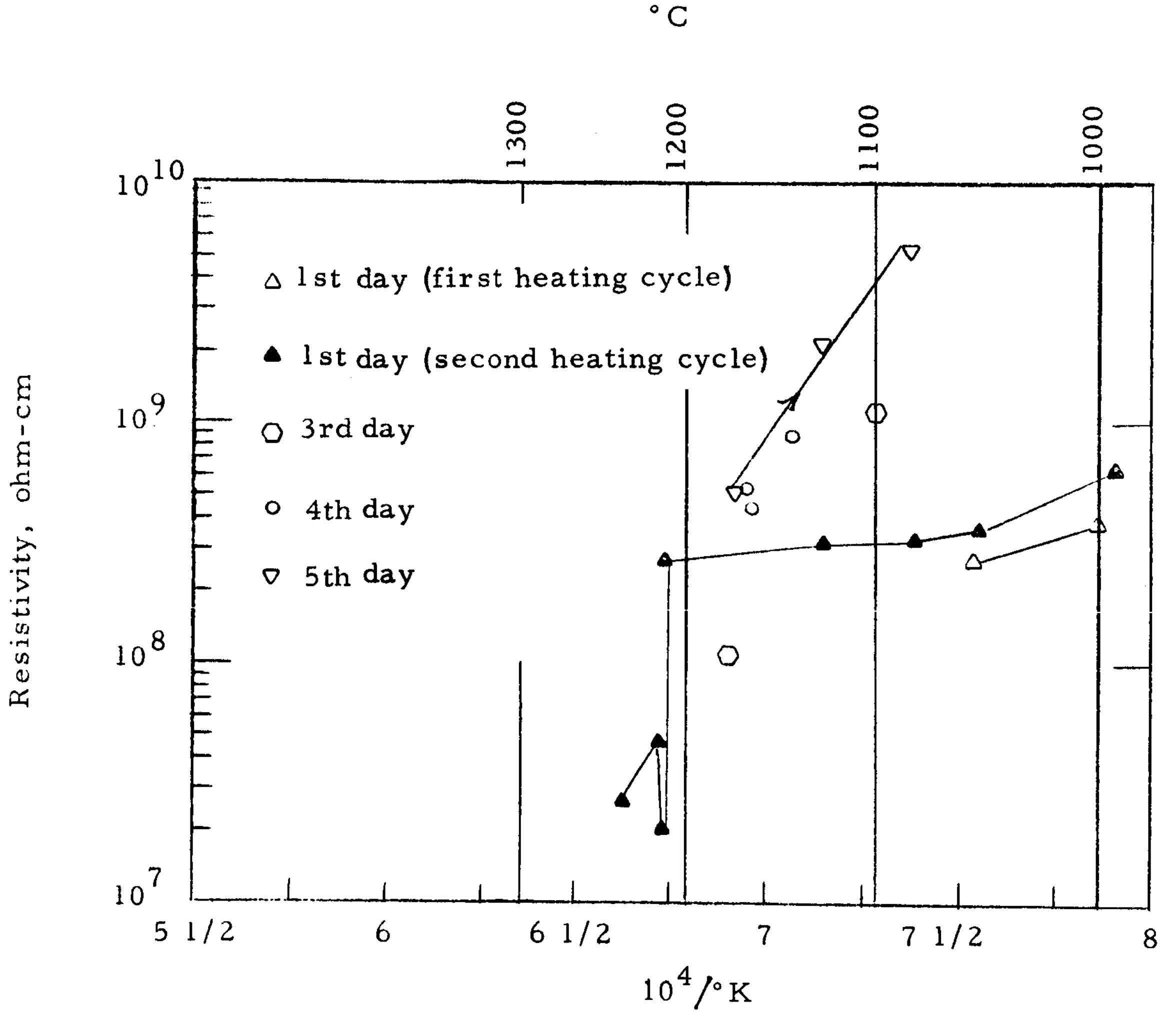


FIG. 35 - DC RESISTIVITY OF ALUCER ALUMINA (3/8 INCH DIAMETER BY 1/8 INCH THICK) IN MERCURY VAPOR WITH HYDROGEN-ARGON CARRIER--100-HOUR TEST. Mercury at 118°C. Tungsten electrodes at 90 V. Molybdenum susceptor.

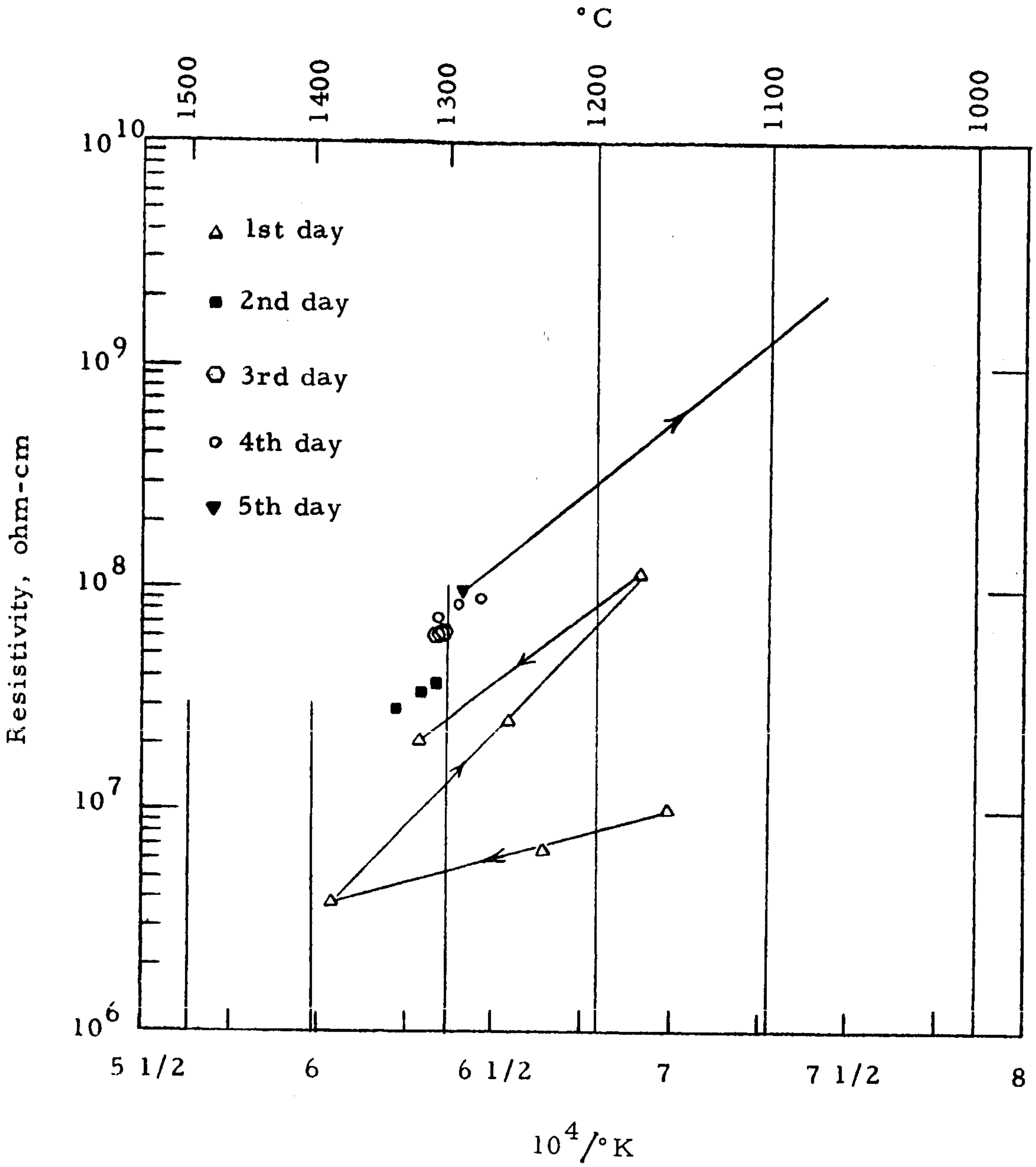


FIG. 36 - DC RESISTIVITY OF ALUCER ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN CESIUM VAPOR WITH HYDROGEN-ARGON CARRIER. 100-hour test. Cesium at 74°C. Tungsten electrodes at 90 V. Molybdenum susceptor.

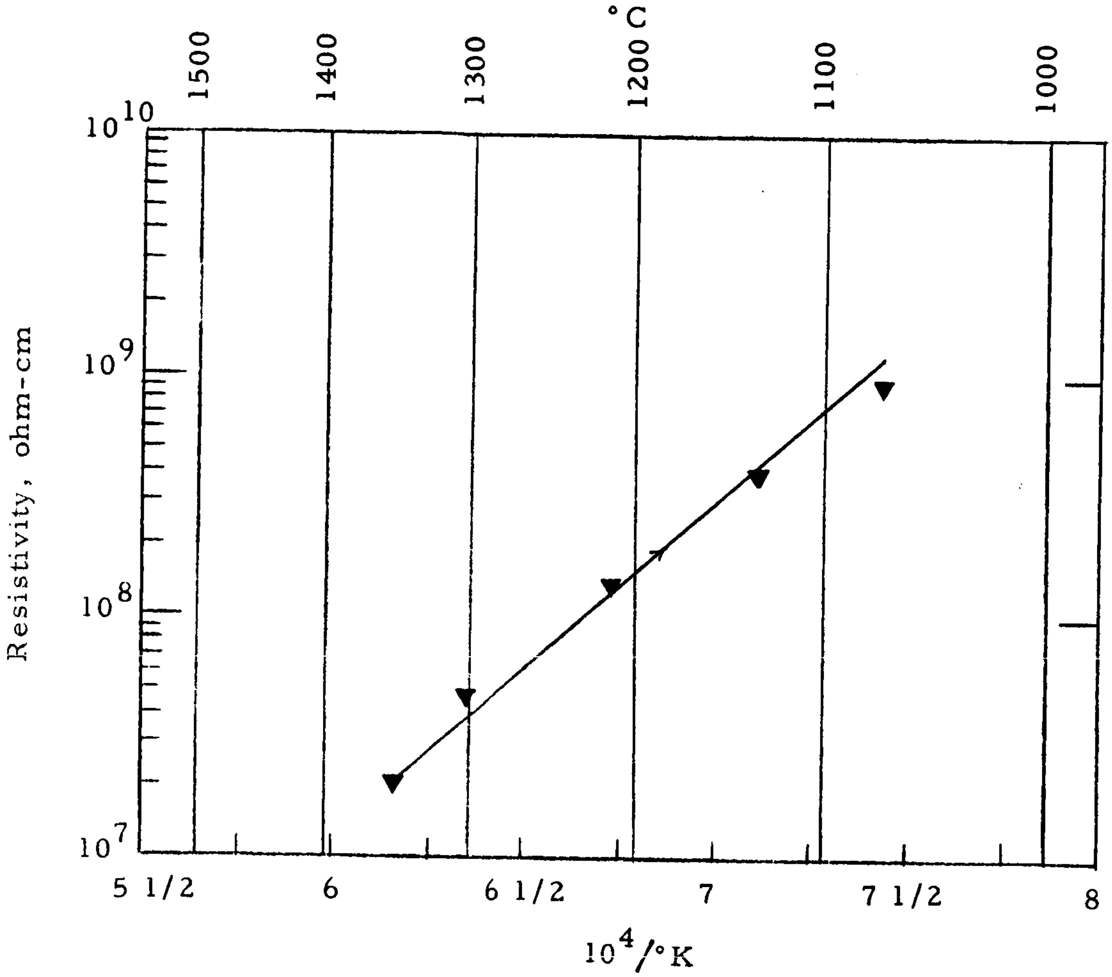


FIG. 37 - DC RESISTIVITY OF ALUCER ALUMINA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN CESIUM VAPOR WITH NITROGEN CARRIER. Cesium at 74°C. Tungsten electrodes at 90 V. Platinum susceptor.

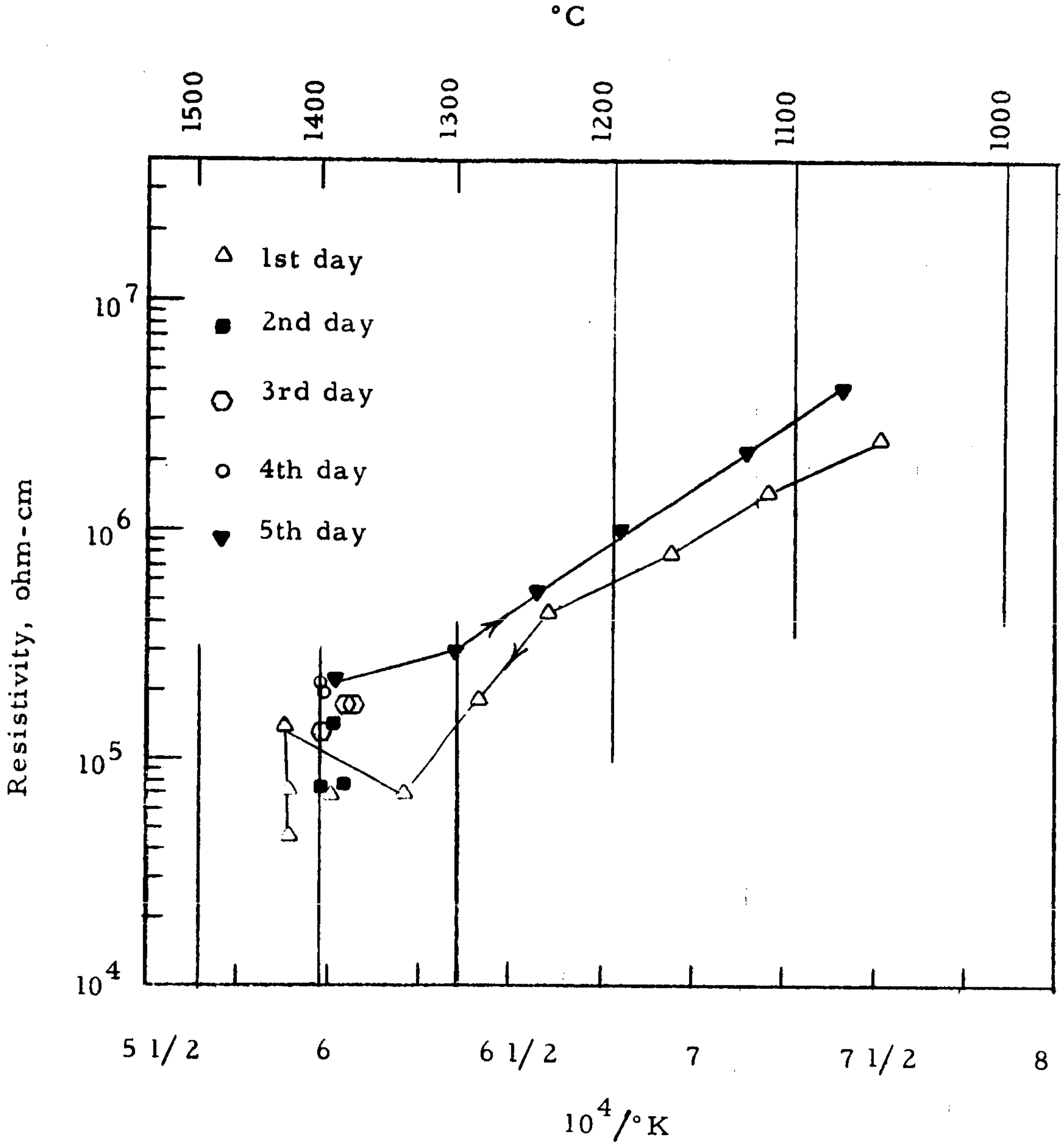


FIG. 38 - DC RESISTIVITY OF MAGNESIA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN PREPURIFIED NITROGEN CONTAINING 500 PPM HYDROGEN--100-HOUR TEST. Tungsten electrodes at 90 V. Platinum susceptor.

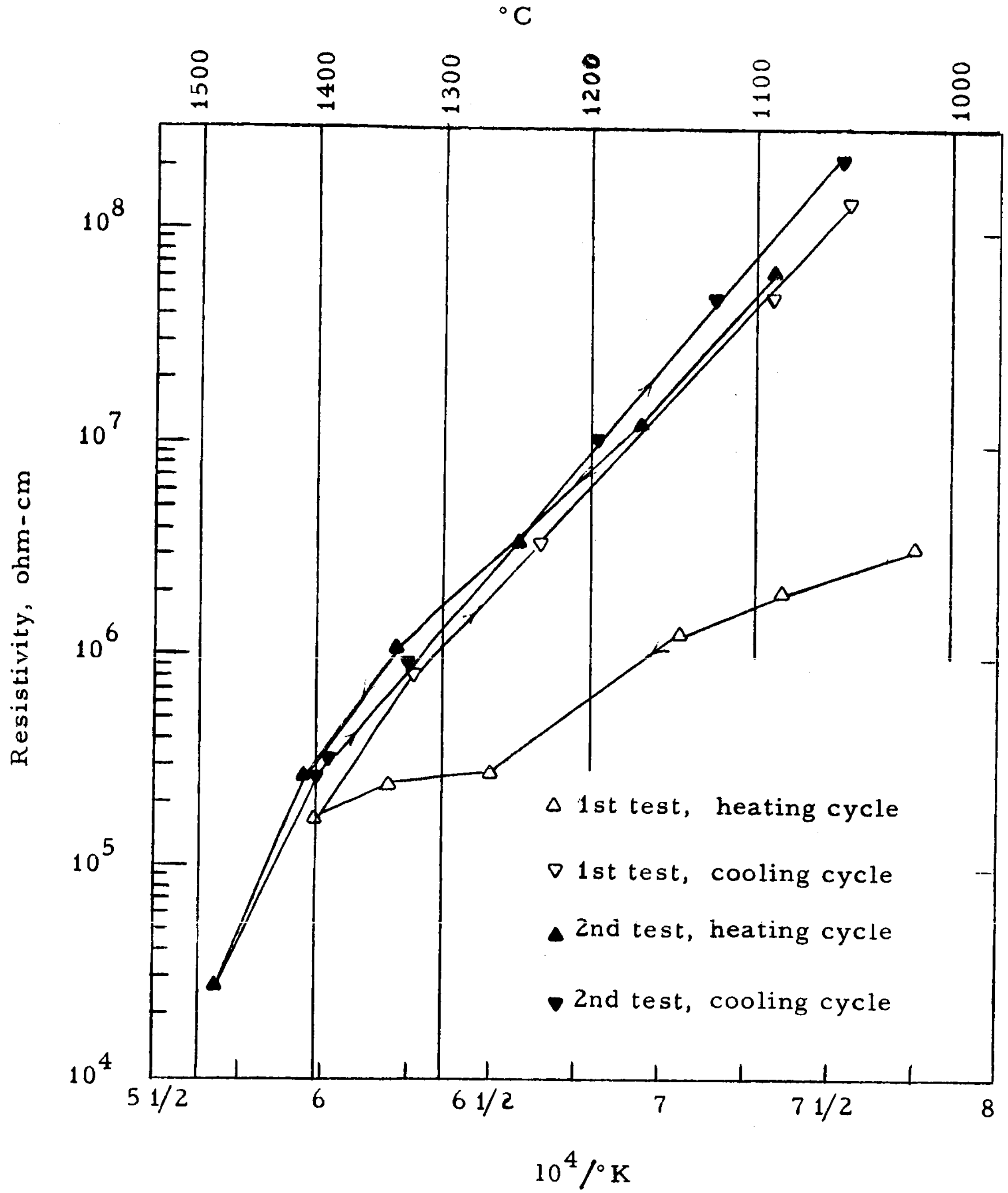


FIG. 39 - DC RESISTIVITY OF MAGNESIA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN PREPURIFIED NITROGEN CONTAINING 500 PPM HYDROGEN--TWO TESTS. Tungsten electrodes at 90 V. Platinum susceptor.

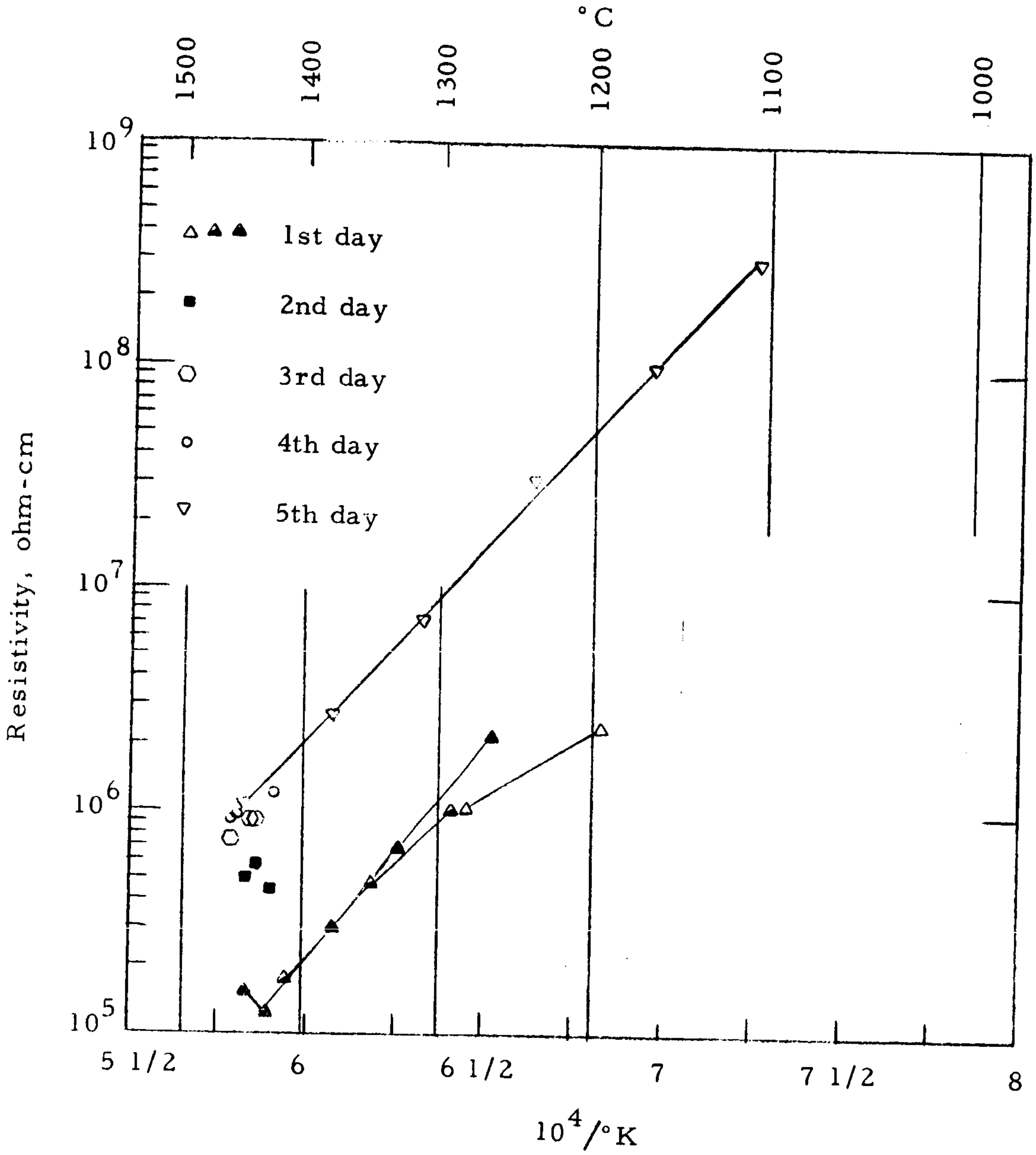


FIG. 40 - DC RESISTIVITY OF MAGNESIA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN NITROGEN-2% HYDROGEN. 100-hour test. Tungsten electrodes at 90 V. Platinum susceptor.

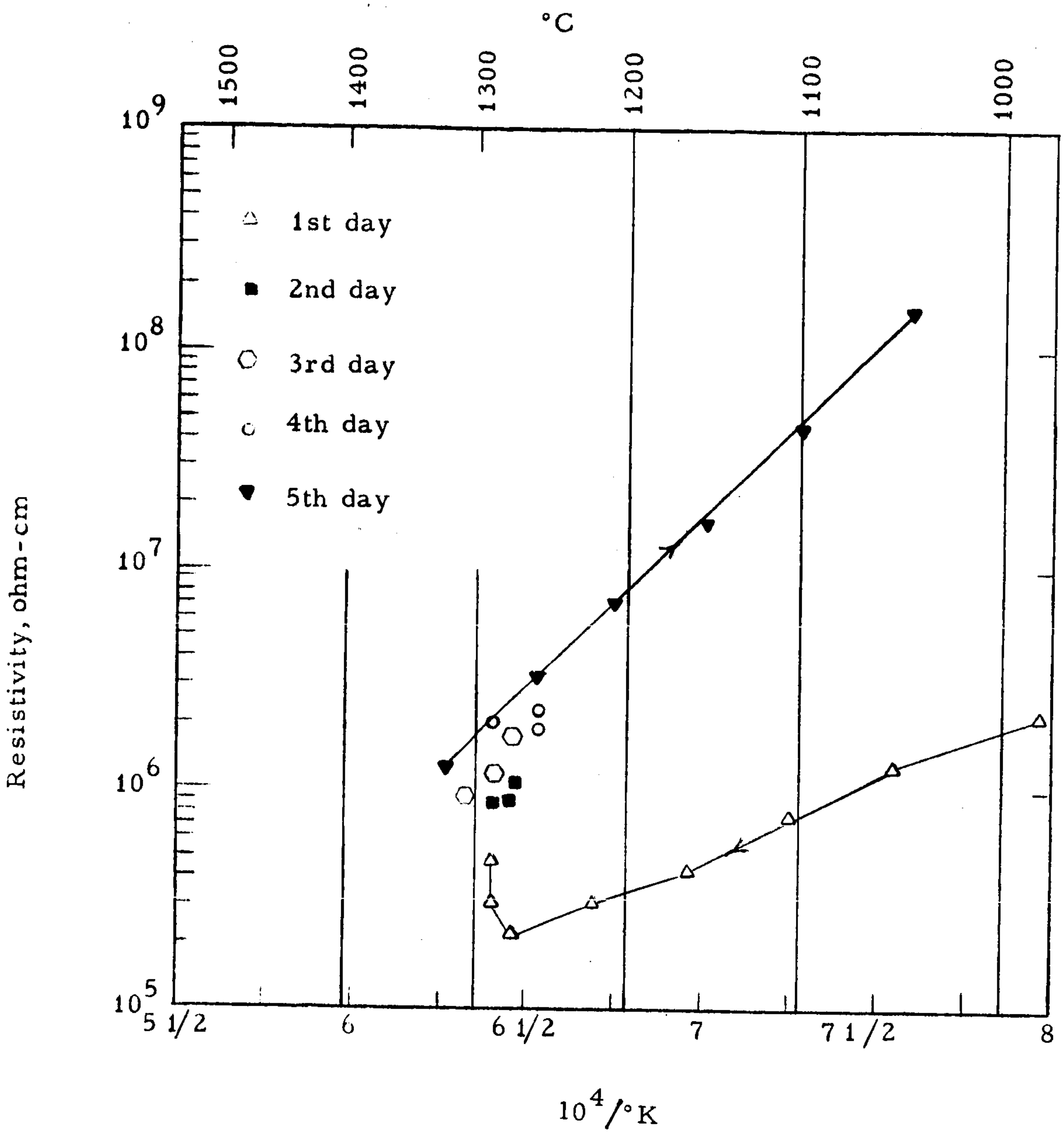


FIG. 41 - DC RESISTIVITY OF MAGNESIA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN HYDROGEN-ARGON--100-HOUR TEST. Tungsten electrodes at 90 V. Molybdenum susceptor.

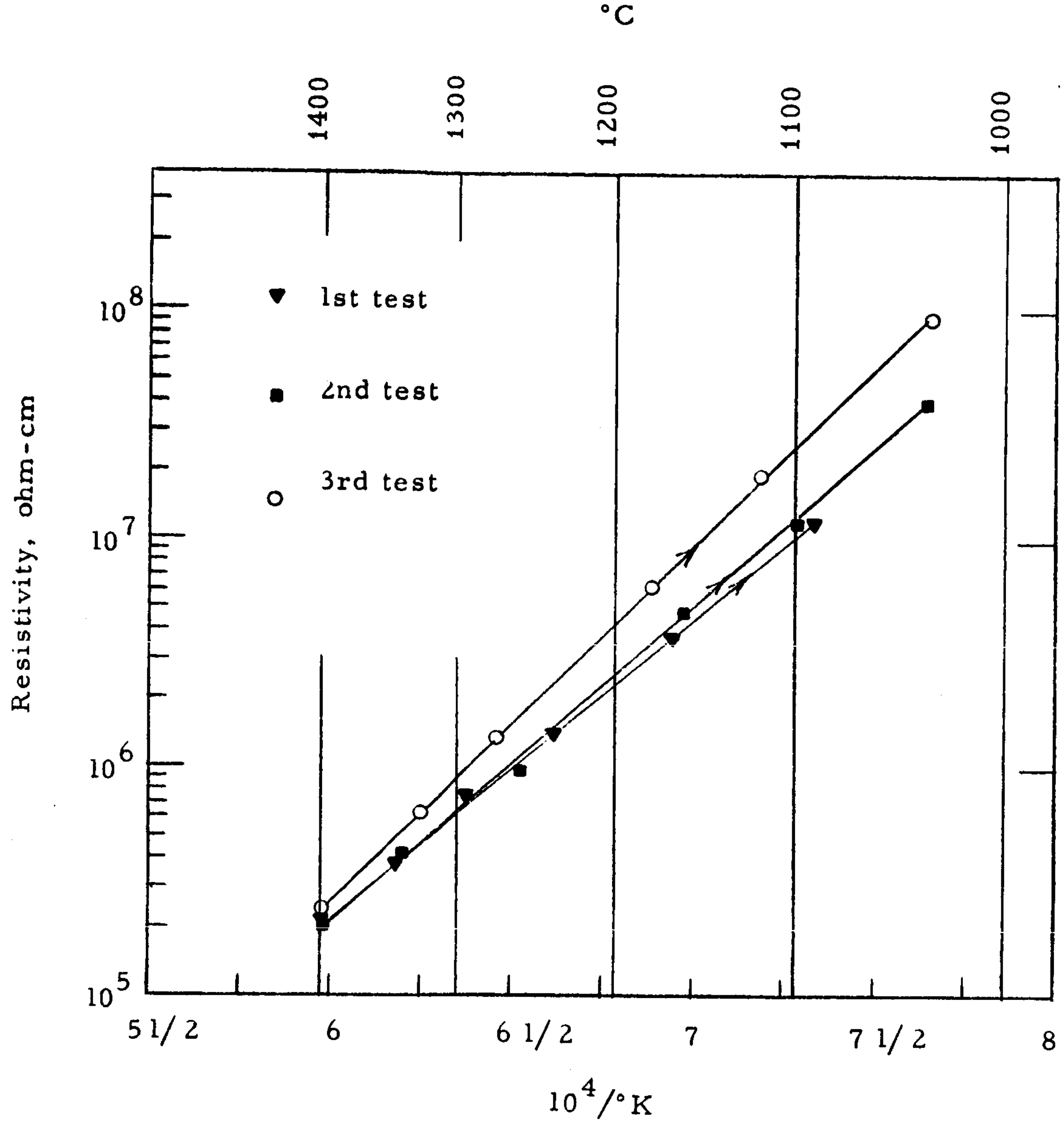


FIG. 42 - DC RESISTIVITY OF MAGNESIA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN HYDROGEN-ARGON--COOLING CYCLE. Tungsten electrodes at 90 V. Molybdenum susceptor.

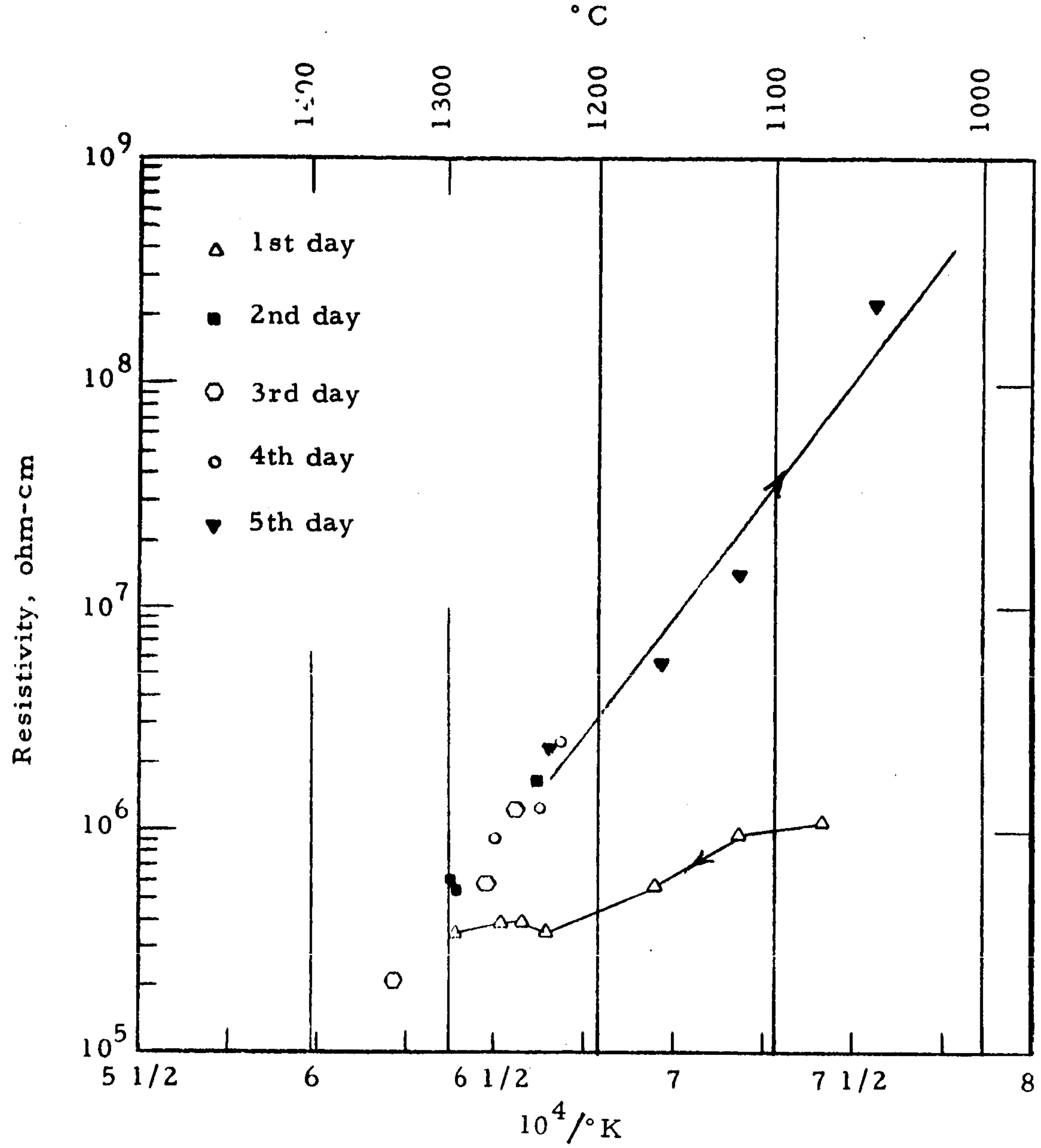


FIG. 43 - DC RESISTIVITY OF MAGNESIA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN MERCURY VAPOR WITH HYDROGEN-ARGON CARRIER--100-HOUR TEST. Mercury at 115°C. Tungsten electrodes at 90 V. Molybdenum susceptor.

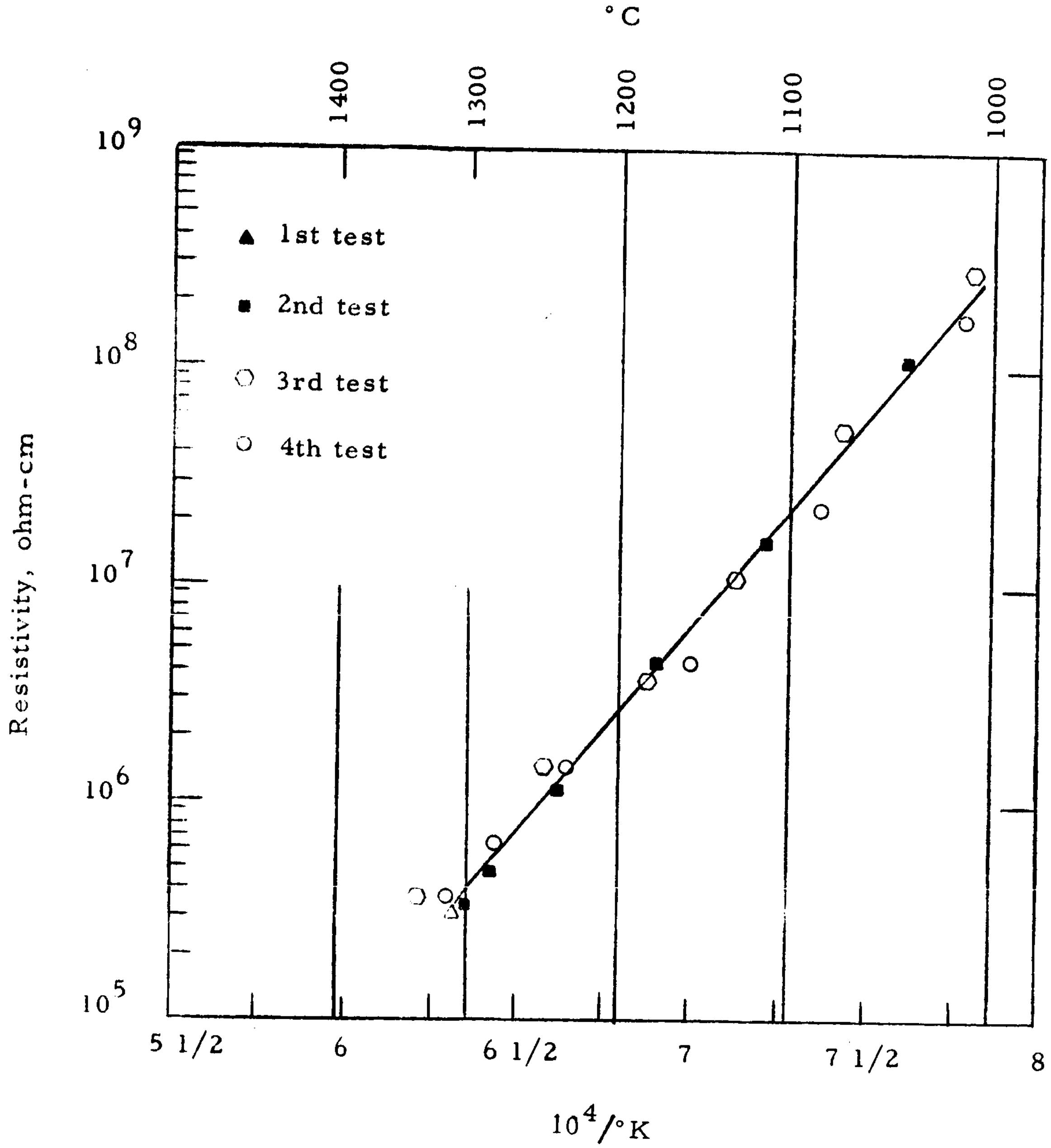


FIG. 44 - DC RESISTIVITY OF MAGNESIA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN MERCURY VAPOR WITH HYDROGEN-ARGON CARRIER--COOLING CYCLE CURVE. Mercury at 116°-125°C. Tungsten electrodes at 90 V. Molybdenum susceptor.

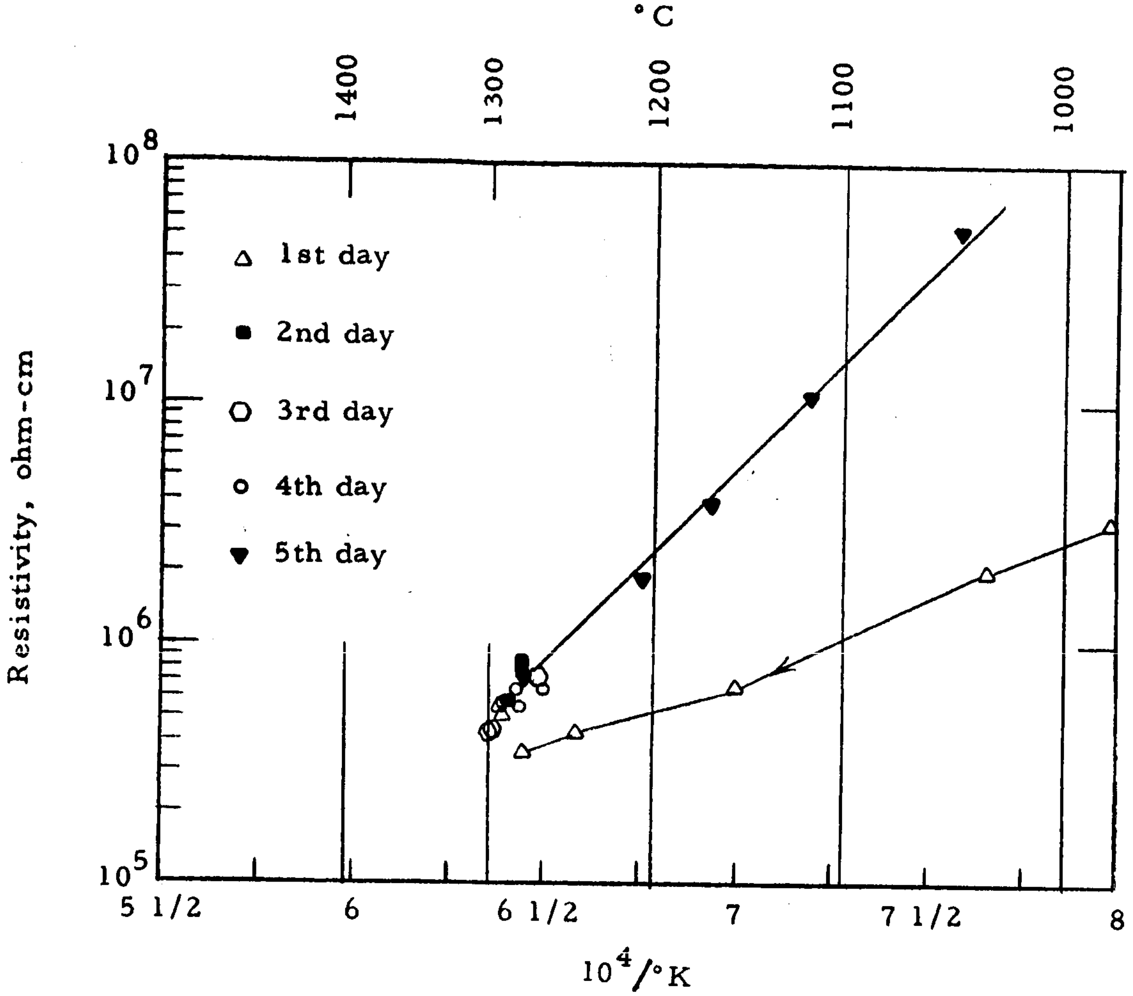


FIG. 45 - DC RESISTIVITY OF MAGNESIA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN CESIUM VAPOR WITH HYDROGEN-ARGON CARRIER--100-HOUR TEST. Cesium at 72°C. Tungsten electrodes at 90 V. Molybdenum susceptor.

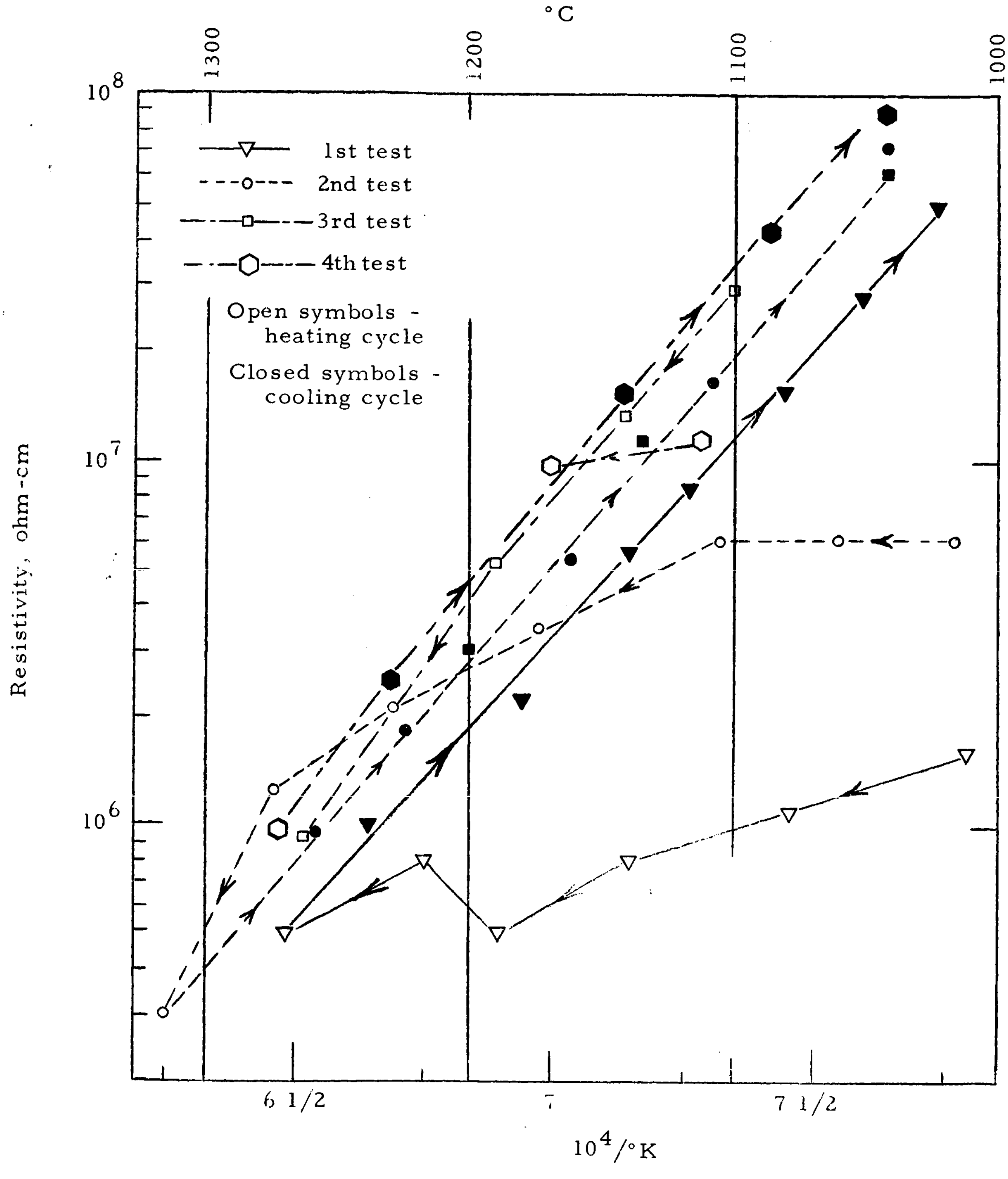


FIG. 46 - DC RESISTIVITY OF MAGNESIA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN CESIUM VAPOR WITH HYDROGEN-ARGON CARRIER--SUMMARY OF COOLING AND HEATING CYCLE CURVES. Tungsten electrodes at 90 V. Molybdenum susceptor.

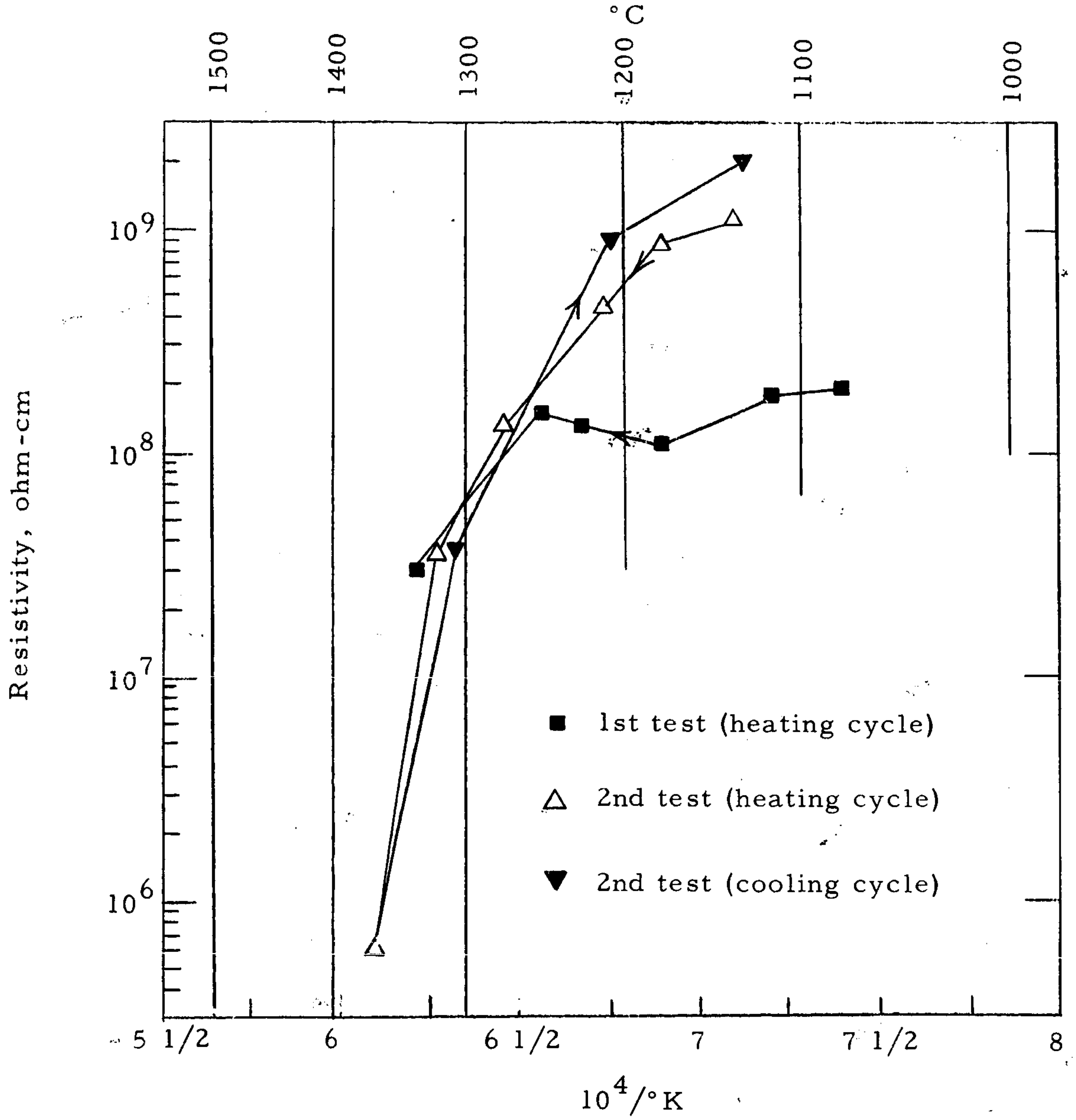


FIG. 47 - DC RESISTIVITY OF BERYLLIA (3/8 INCH DIAMETER BY 1/8 INCH THICK) IN PREPURIFIED NITROGEN CONTAINING 500 PPM HYDROGEN. Tungsten electrodes at 90 V. Platinum susceptor.

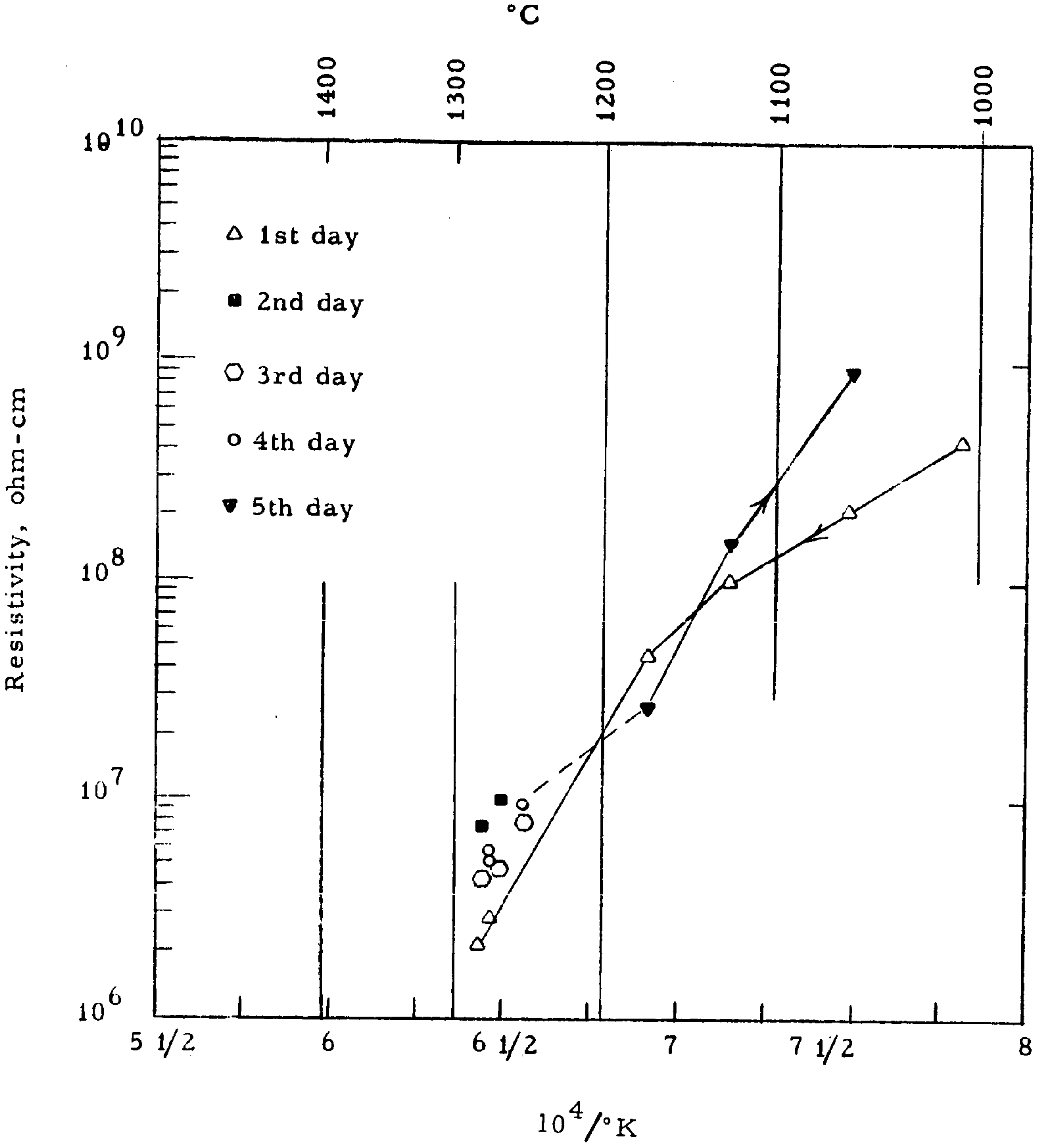


FIG. 48 - DC RESISTIVITY OF BERYLLIA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN HYDROGEN-ARGON. 100-hour test. Tungsten electrodes at 90 V. Molybdenum susceptor.

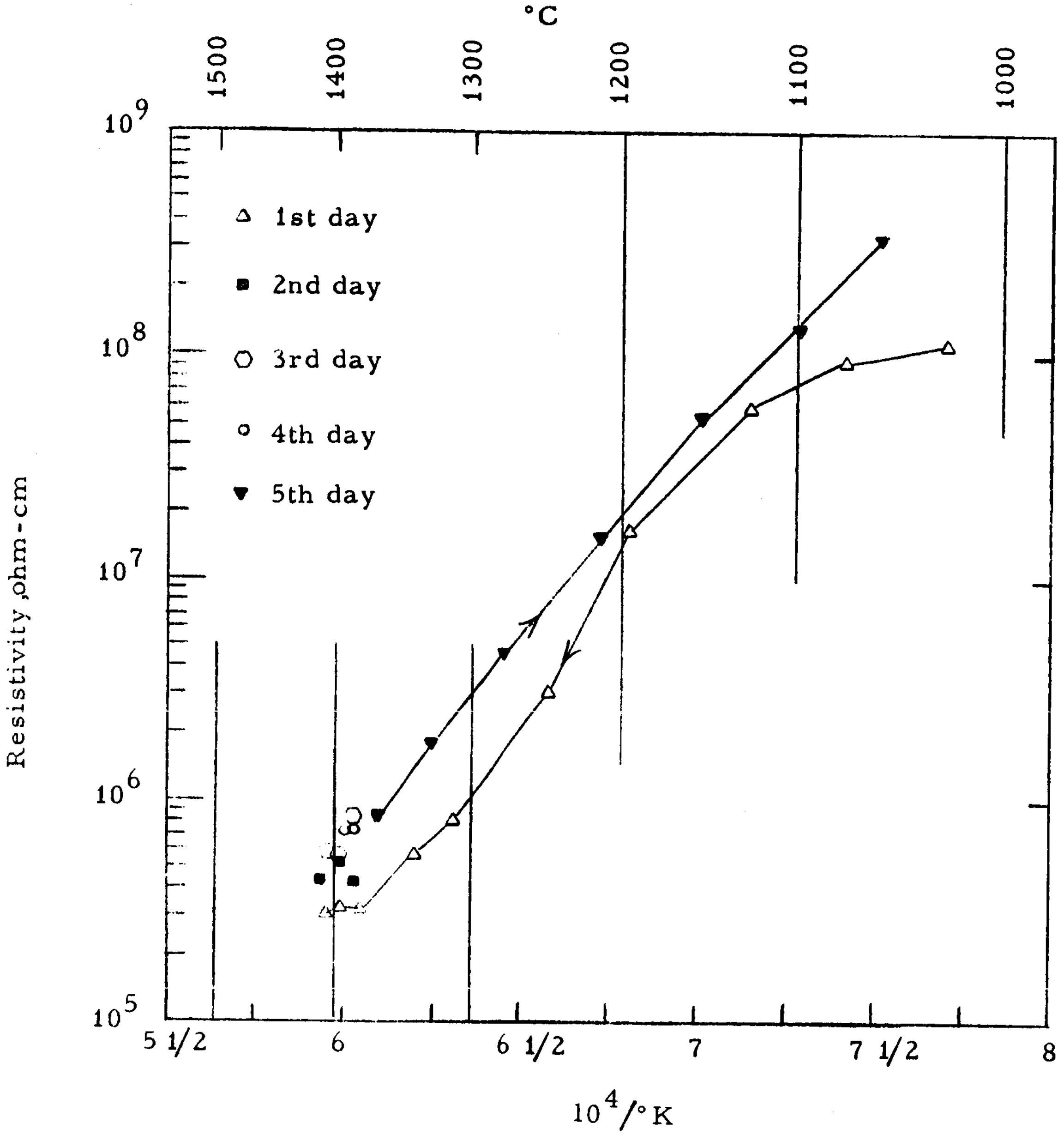


FIG. 49 - DC RESISTIVITY OF BERYLLIA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN HYDROGEN-ARGON. 100-hour test. Tungsten electrodes at 90 V. Graphite susceptor. Sample previously tested with molybdenum susceptor for 100 hours.

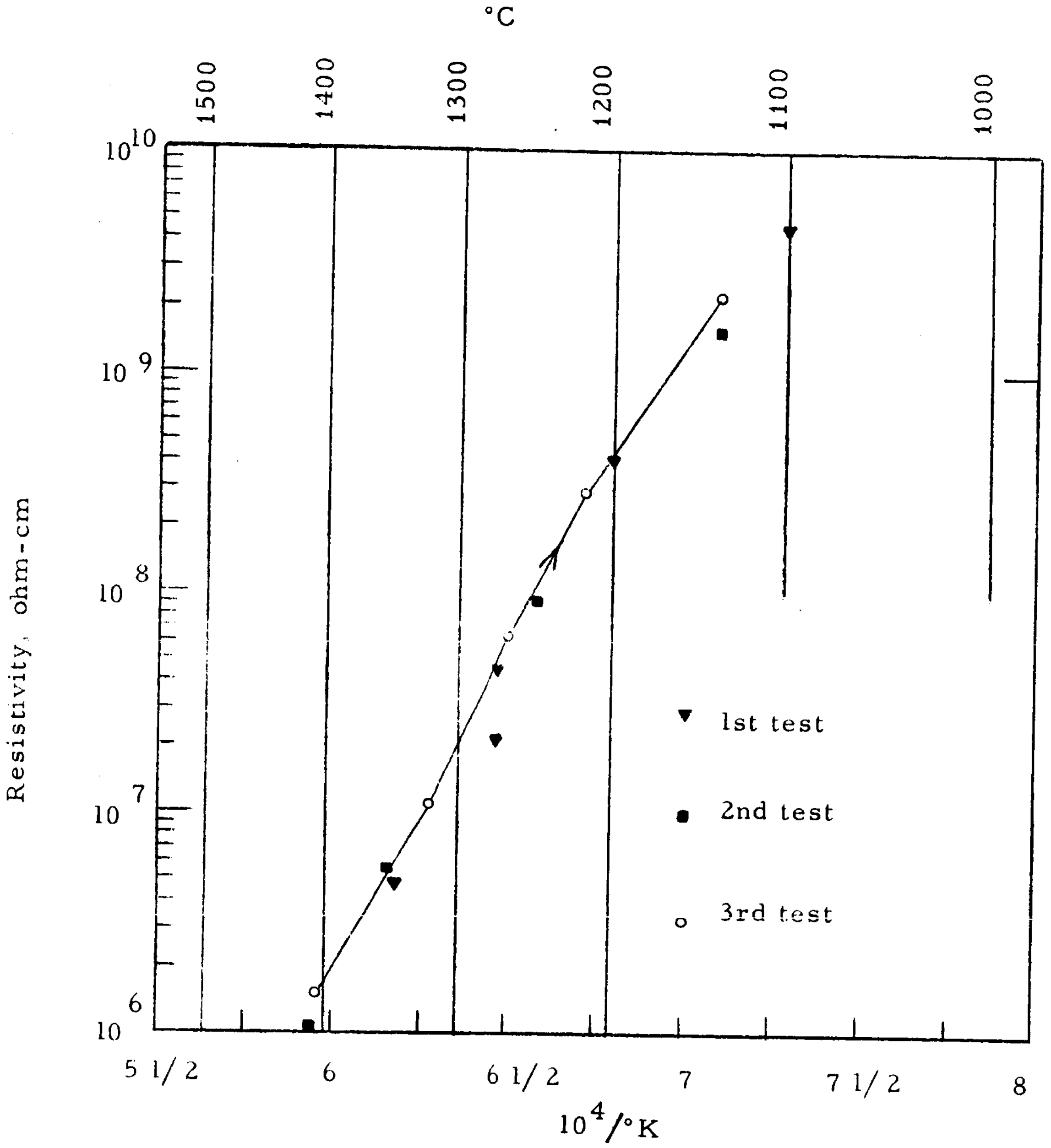


FIG. 50 - DC RESISTIVITY OF BERYLLIA (3/8 INCH DIAMETER BY 1/8 INCH THICK) IN HYDROGEN-ARGON--SUMMARY OF COOLING CYCLE CURVE. Tungsten electrodes at 90 V. Molybdenum susceptor.

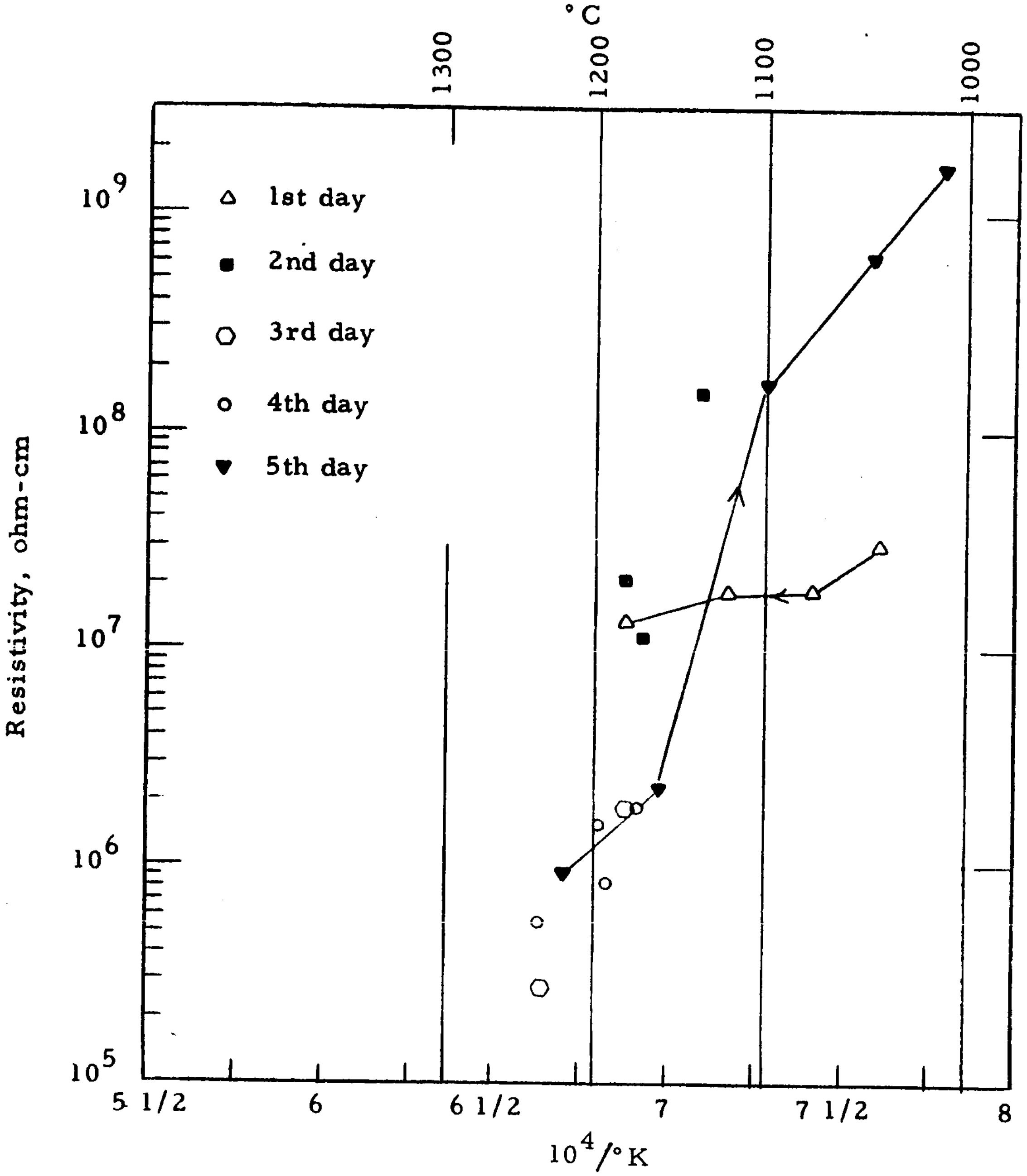


FIG. 51 - DC RESISTIVITY OF BERYLLIA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN MERCURY VAPOR WITH HYDROGEN-ARGON CARRIER. 100-hour test. Mercury at 115°C. Tungsten electrodes at 90 V. Molybdenum susceptor.

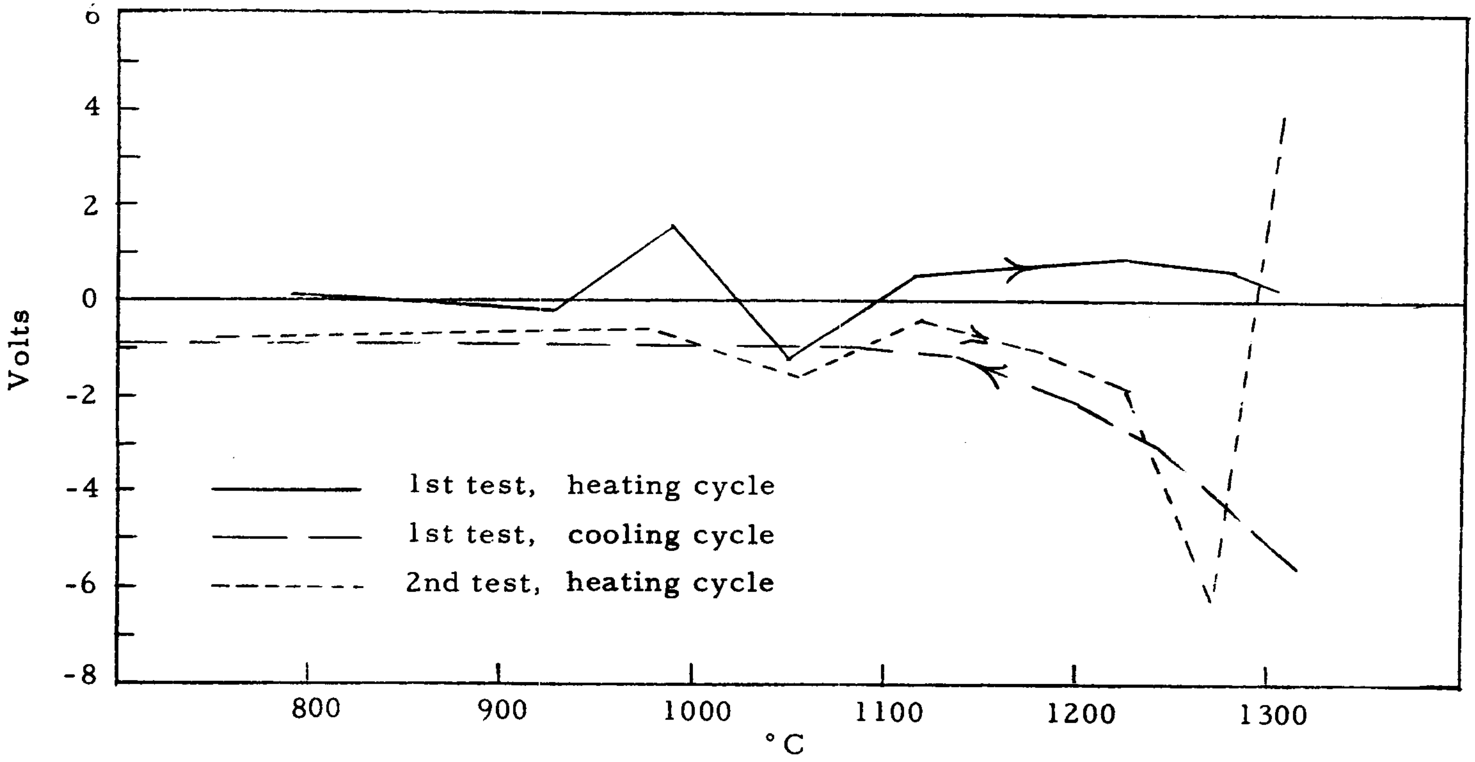


FIG. 52 - OPEN-CIRCUIT EMF ACROSS BERYLLIA (3/8 INCH DIAMETER BY 1/8 INCH THICK) IN MERCURY VAPOR WITH HYDROGEN-ARGON CARRIER. In 1st test, 90 V were applied to the sample three separate times at maximum temperature. Tungsten electrodes. Molybdenum susceptor.

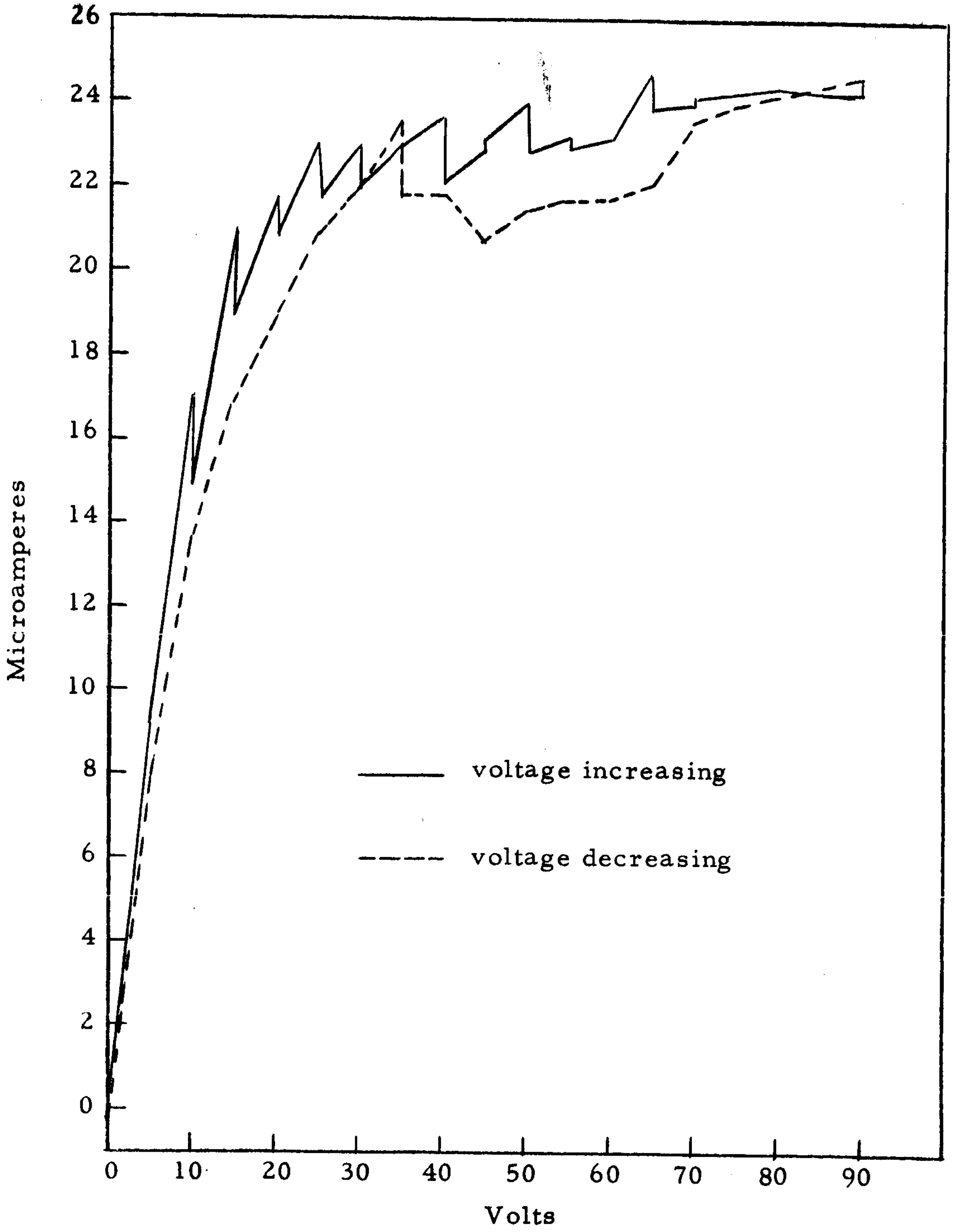


FIG. 53 - CURRENT VS. VOLTAGE FOR BERYLLIA (3/8 INCH DIAMETER BY 1/8 INCH THICK) IN MERCURY VAPOR WITH HYDROGEN-ARGON CARRIER. Temperature 1305-1315°C. First test, mercury at 119°C. Measurements made after sample was heated to temperature without an applied voltage. Tungsten electrodes. Molybdenum susceptor.

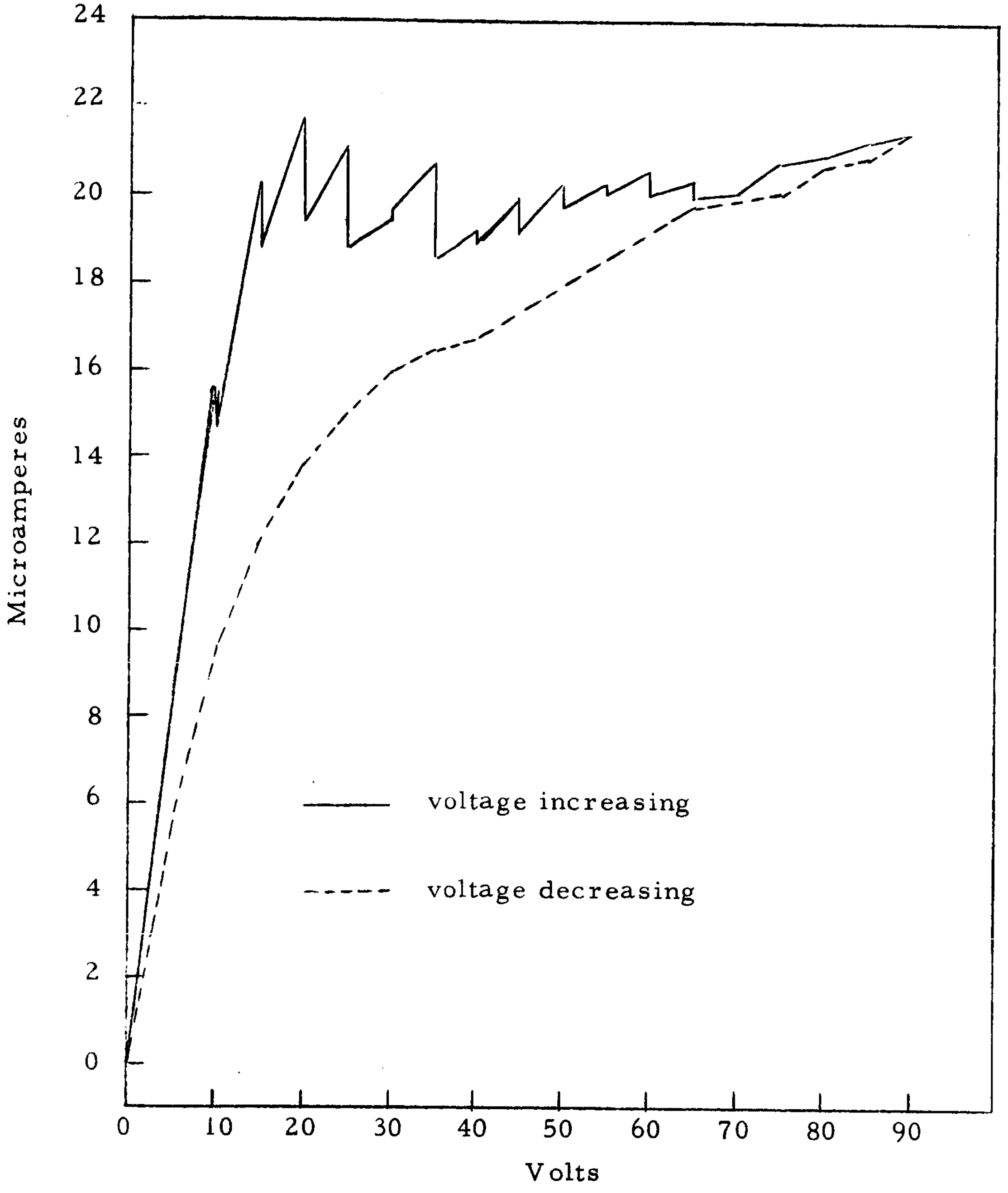


FIG. 54 - CURRENT VS. VOLTAGE FOR BERYLLIA (3/8 INCH DIAMETER BY 1/8 INCH THICK) IN MERCURY VAPOR WITH HYDROGEN-ARGON CARRIER. Temperature 1310-1315°C. First test, mercury at 119°C. Measurements made 1 hour after those in Fig. 53. Tungsten electrodes. Molybdenum susceptor.

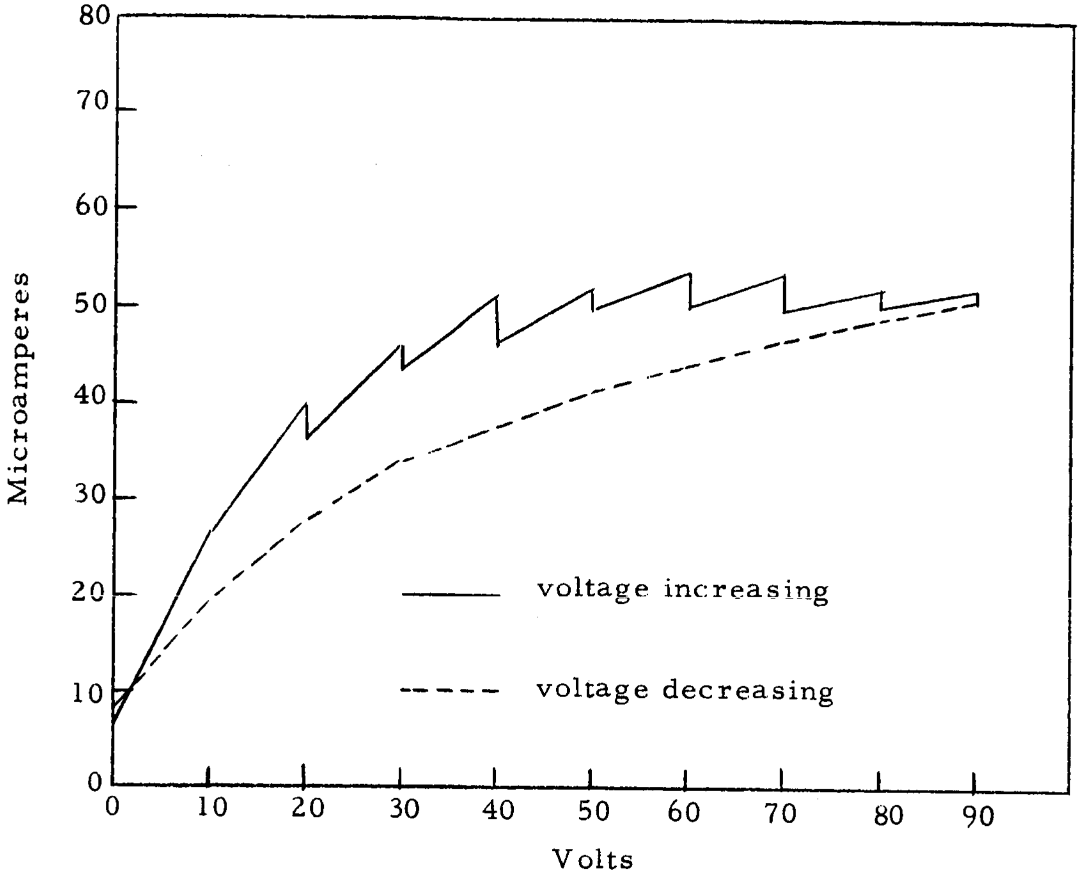


FIG. 55 - CURRENT VS. VOLTAGE FOR BERYLLIA (3/8 INCH DIAMETER BY 1/8 INCH THICK) IN MERCURY VAPOR WITH HYDROGEN-ARGON CARRIER. Temperature 1315°C. First test, mercury at 119°C. Measurements made 3 hours after those in Fig. 53. Tungsten electrodes. Molybdenum susceptor.

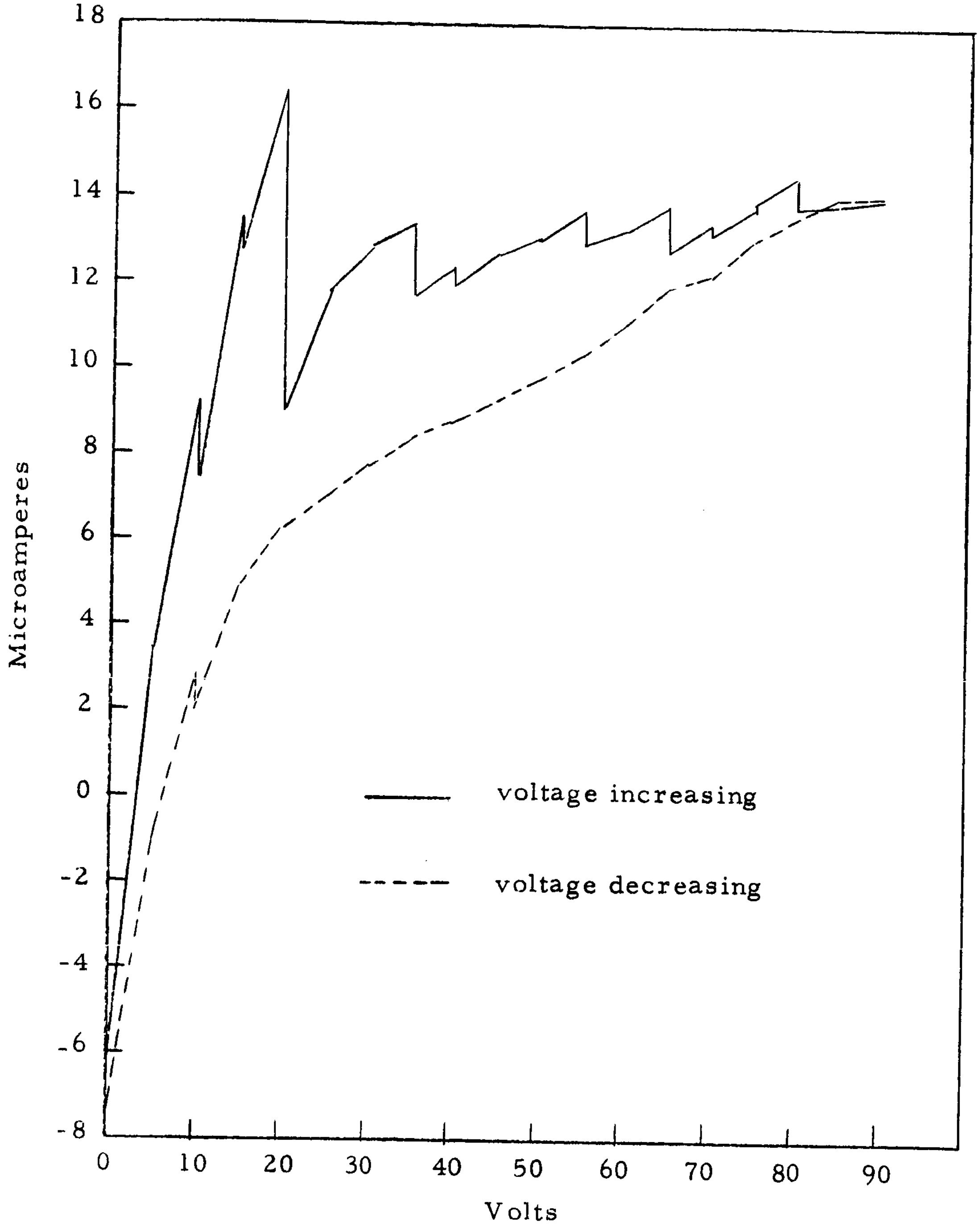


FIG. 56 - CURRENT VS. VOLTAGE FOR BERYLLIA (3/8 INCH DIAMETER BY 1/8 INCH THICK) IN MERCURY VAPOR WITH HYDROGEN-ARGON CARRIER. Temperature 1305-1315°C. Second test, mercury at 121°C. Tungsten electrodes. Molybdenum susceptor.

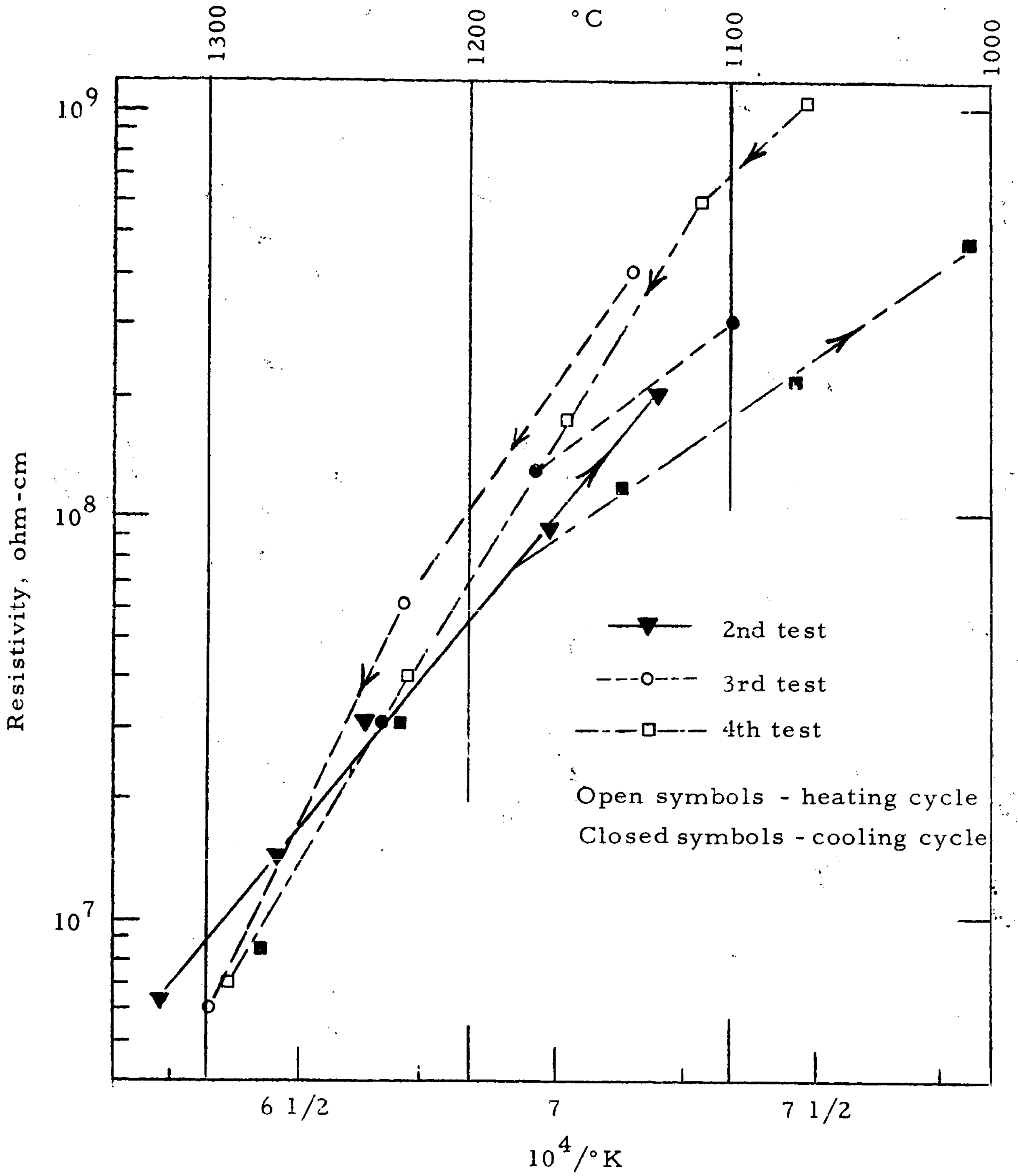


FIG. 57 - DC RESISTIVITY OF BERYLLIA (3/8 INCH DIAMETER BY 1/8 INCH THICK) IN MERCURY VAPOR WITH HYDROGEN-ARGON CARRIER--SUMMARY OF HEATING AND COOLING CYCLE CURVES. Mercury at 120°C. Tungsten electrodes at 90 V. Molybdenum susceptor.

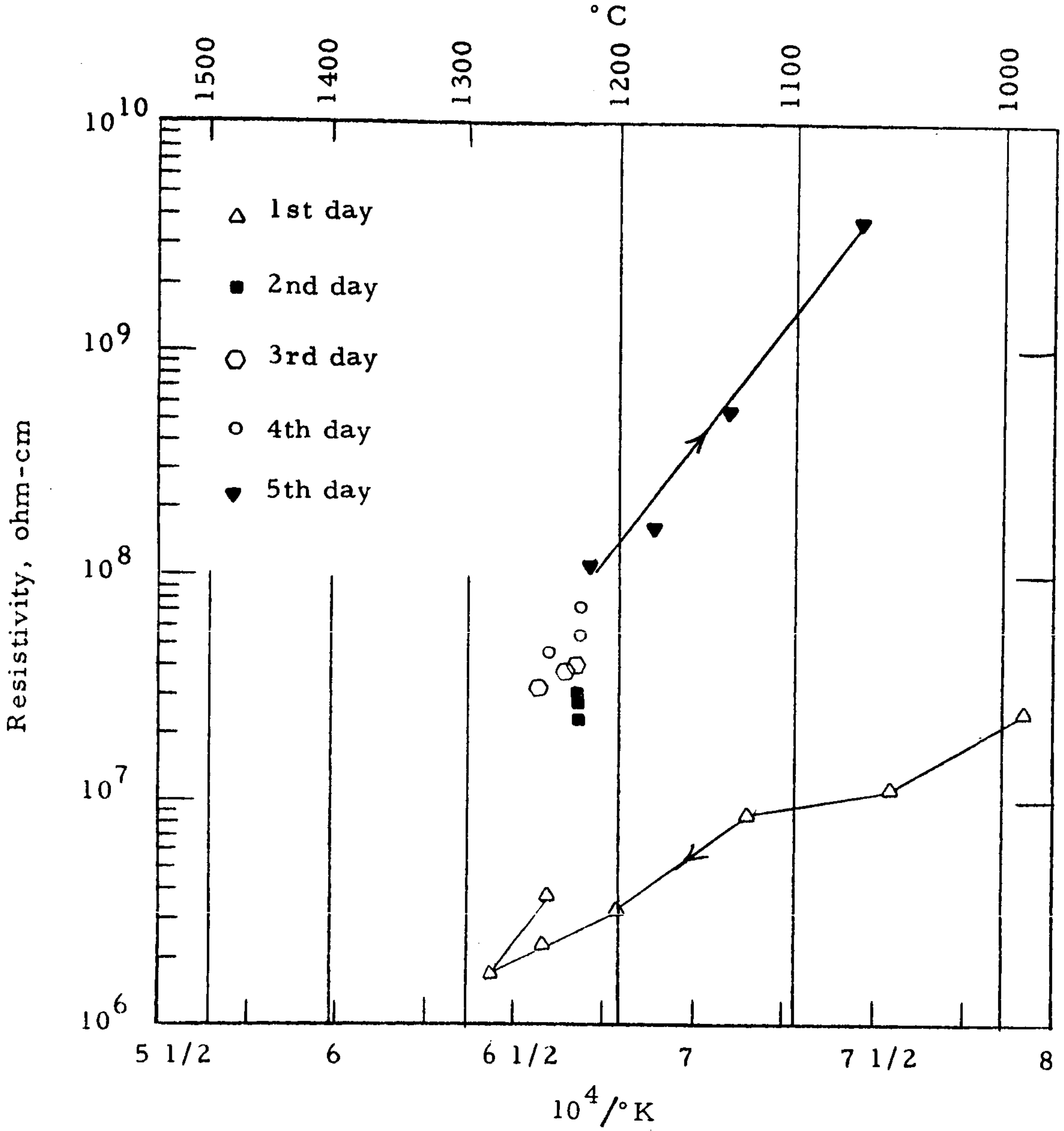


FIG. 58 - DC RESISTIVITY OF BERYLLIA (3/8 INCH DIAMETER BY 1/2 INCH THICK) IN CESIUM VAPOR WITH HYDROGEN-ARGON CARRIER--100-HOUR TEST. Cesium at 74°C. Tungsten electrodes at 90 V. Molybdenum susceptor.

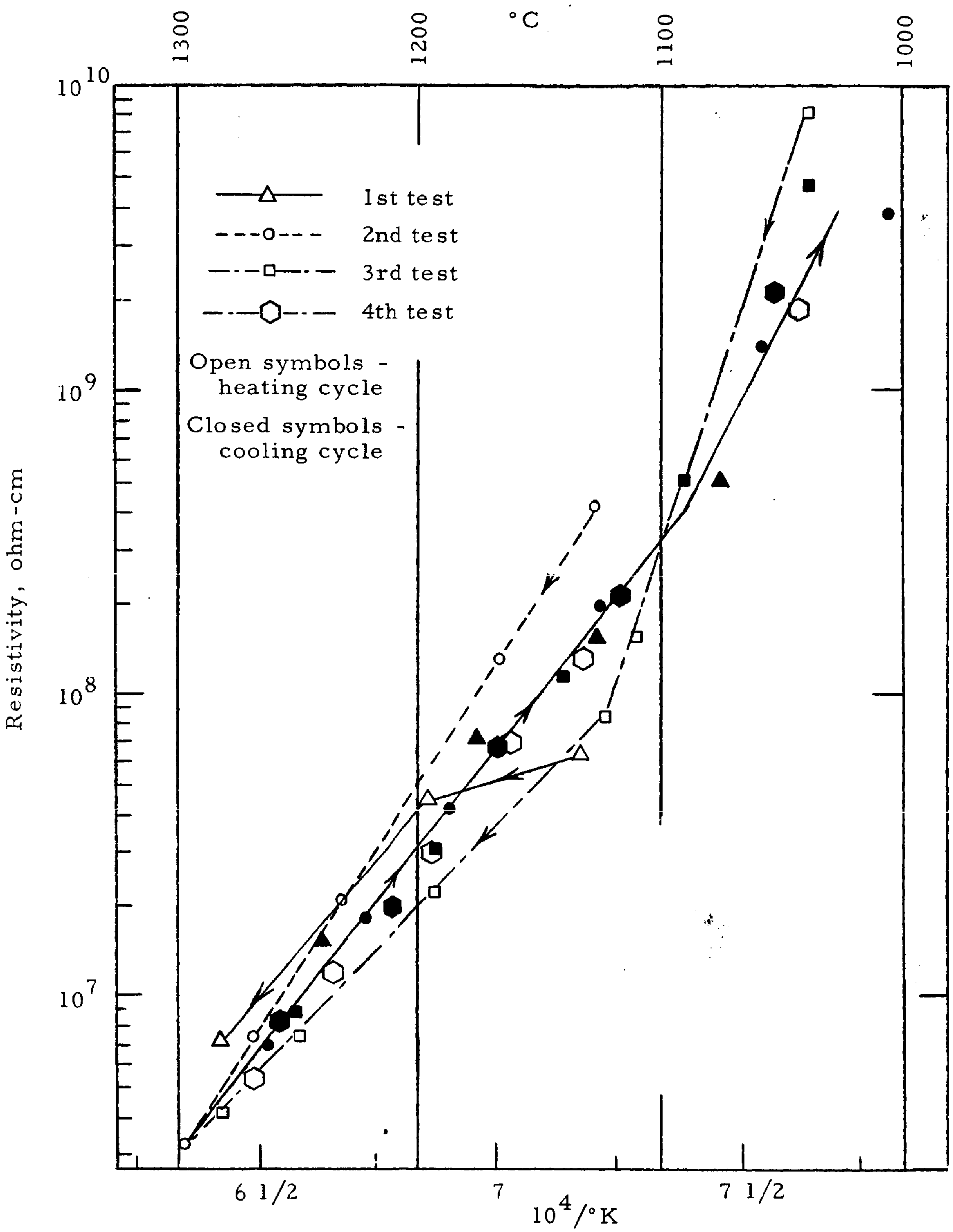


FIG. 59 - DC RESISTIVITY OF BERYLLIA (3/8 INCH DIAMETER BY 1/8 INCH THICK) IN CESIUM VAPOR WITH HYDROGEN-ARGON CARRIER--SUMMARY OF HEATING AND COOLING CYCLE CURVES. Tungsten electrodes at 90 V. Molybdenum susceptor.

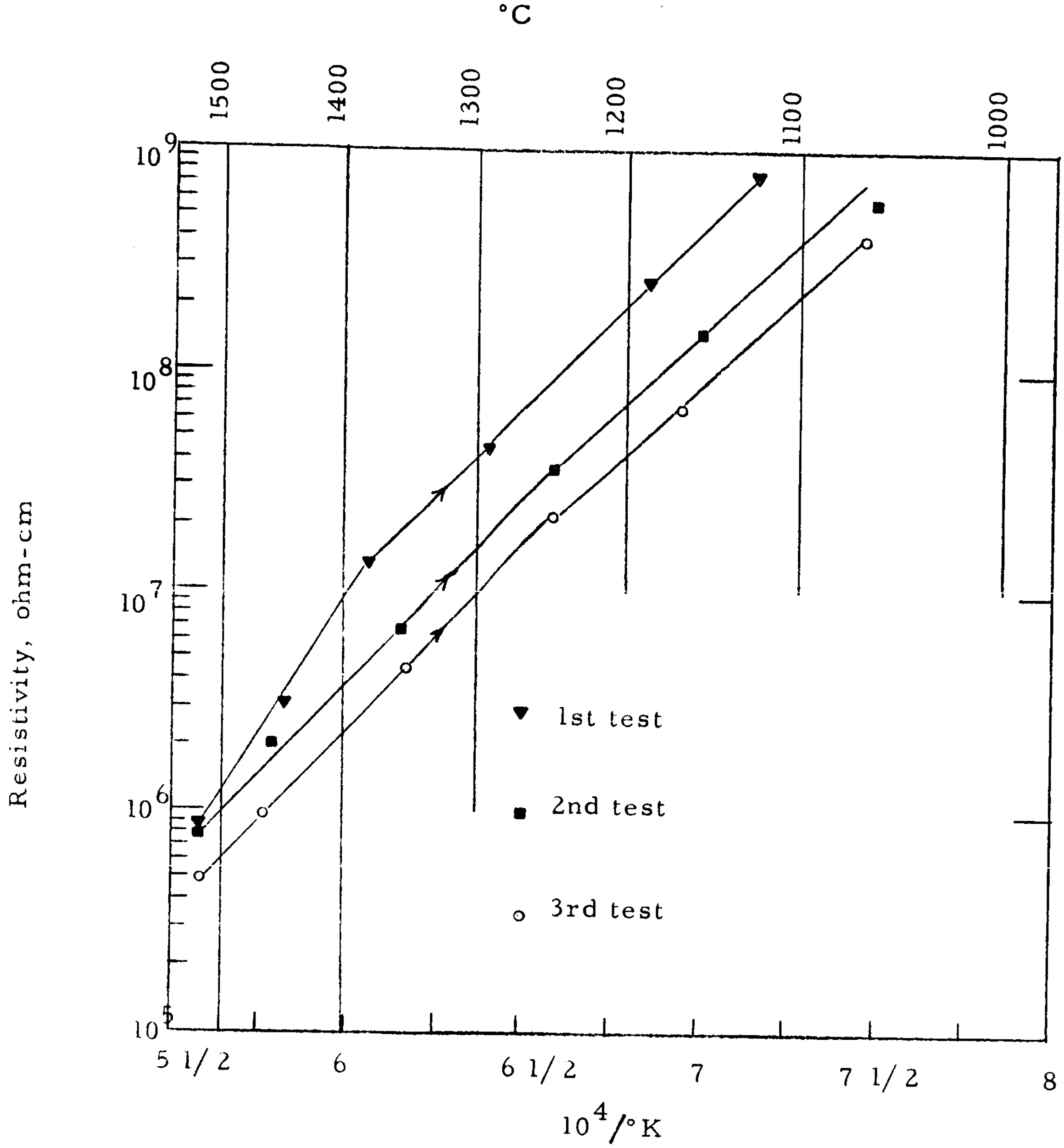


FIG. 60 - DC RESISTIVITY OF PYROLYTIC BORON NITRIDE (3/8 INCH DIAMETER BY 1/8 INCH THICK) IN PREPURIFIED NITROGEN CONTAINING 500 PPM HYDROGEN--COOLING CYCLE CURVES. Tungsten electrodes at 90 V. Platinum susceptor.

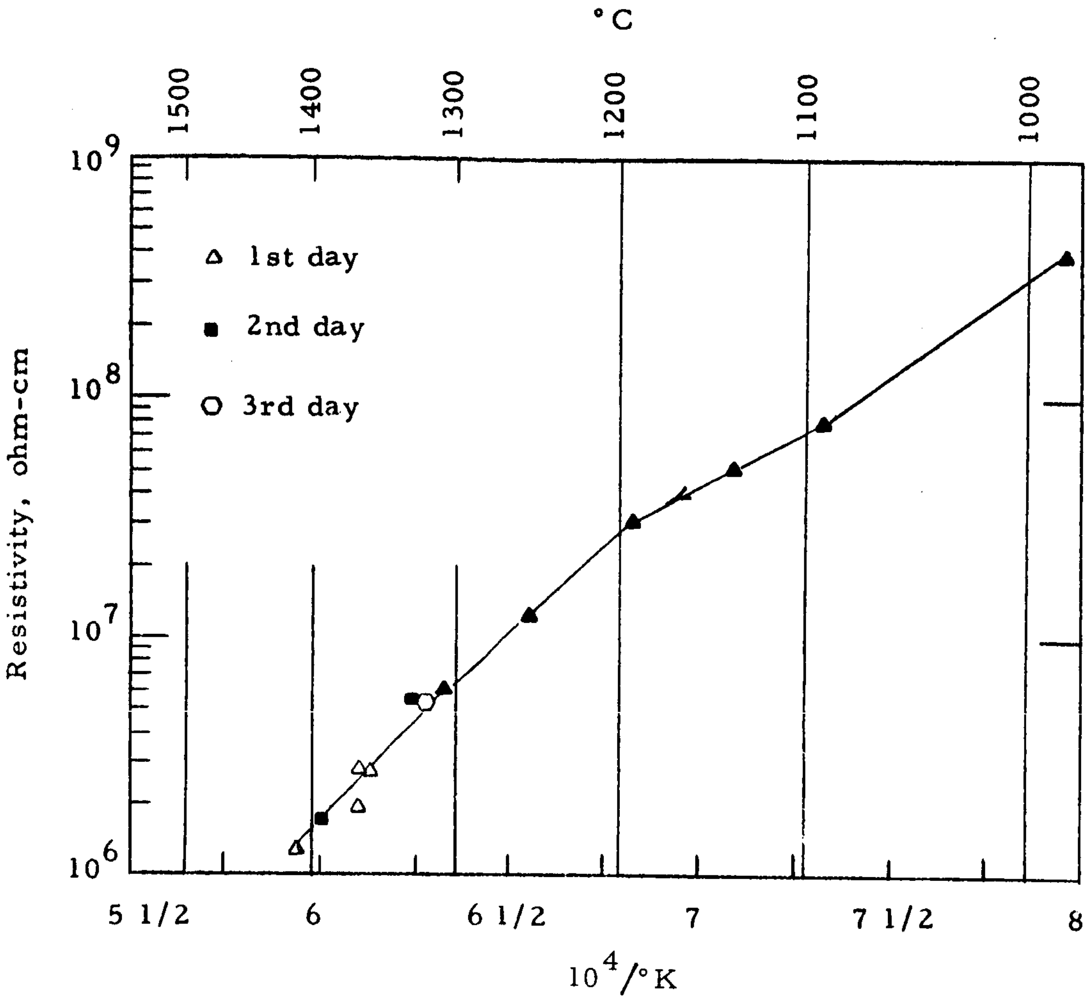


FIG. 61 - DC RESISTIVITY OF PYROLYTIC BORON NITRIDE (3/8 INCH DIAMETER BY 5/32 INCH THICK) IN PREPURIFIED NITROGEN CONTAINING 1000 PPM HYDROGEN. 100-hour test. Tungsten electrodes at 90 V. Platinum susceptor.

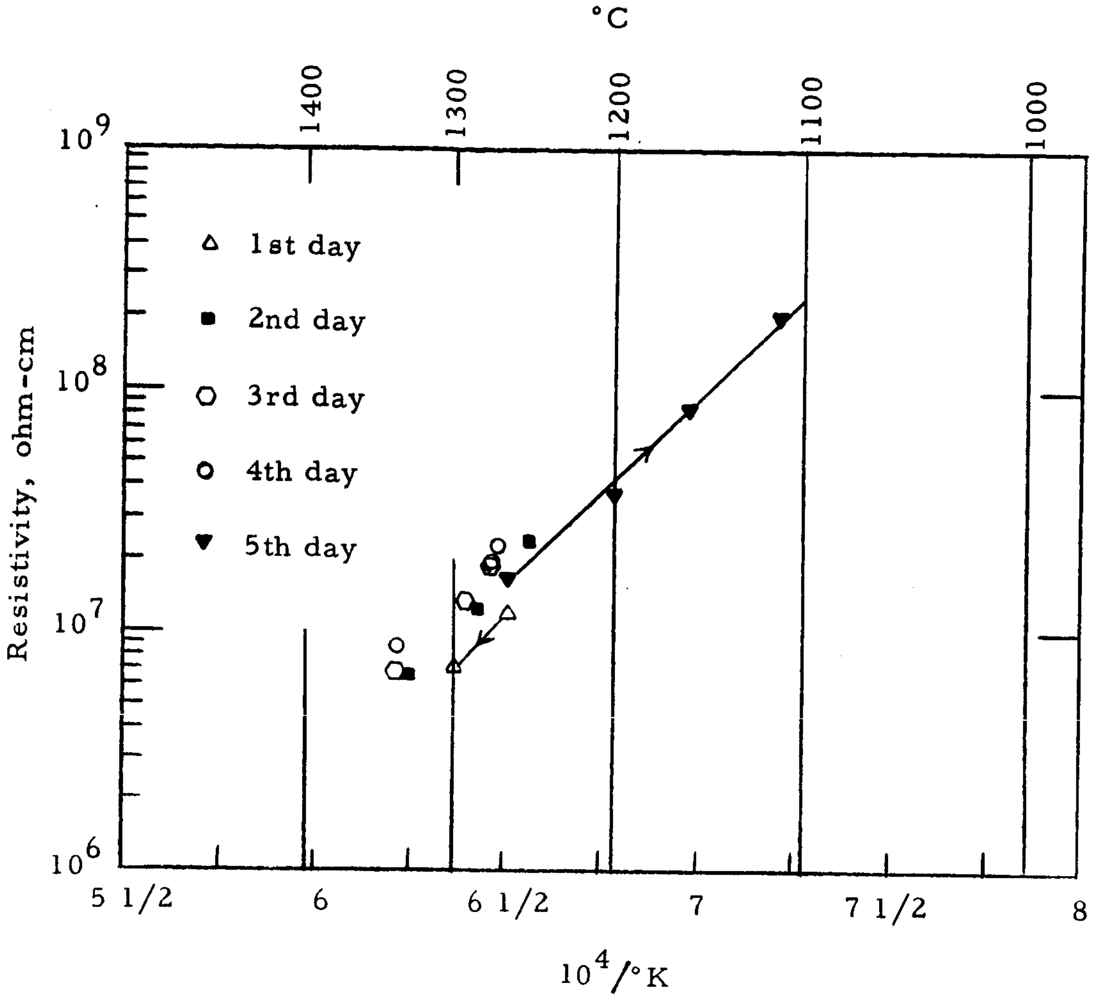


FIG. 62 - DC RESISTIVITY OF PYROLYTIC BORON NITRIDE (3/8 INCH DIAMETER BY 9/64 INCH THICK) IN NITROGEN-2% HYDROGEN. 100-hour test. Tungsten electrodes at 90 V. Molybdenum susceptor.

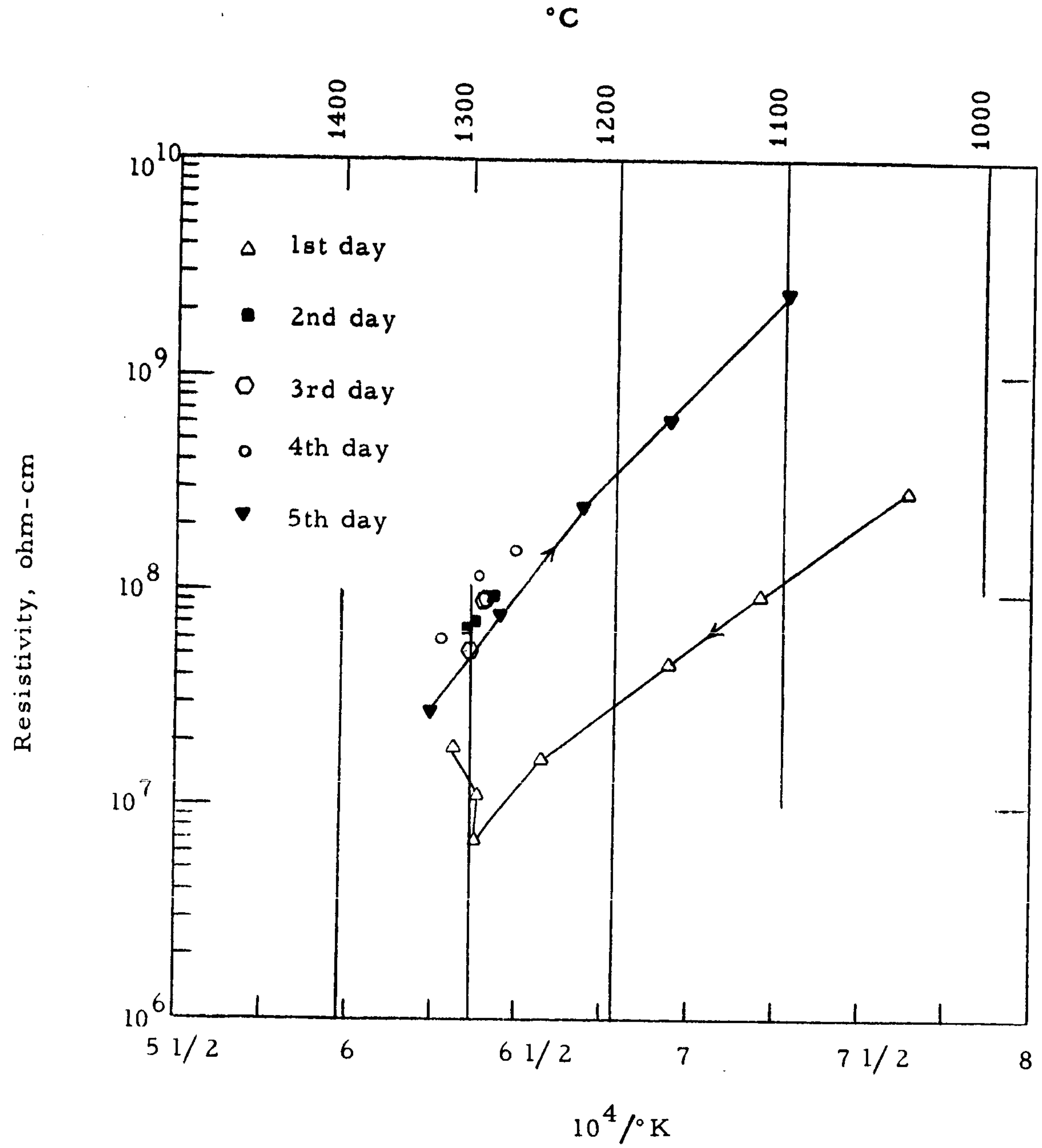
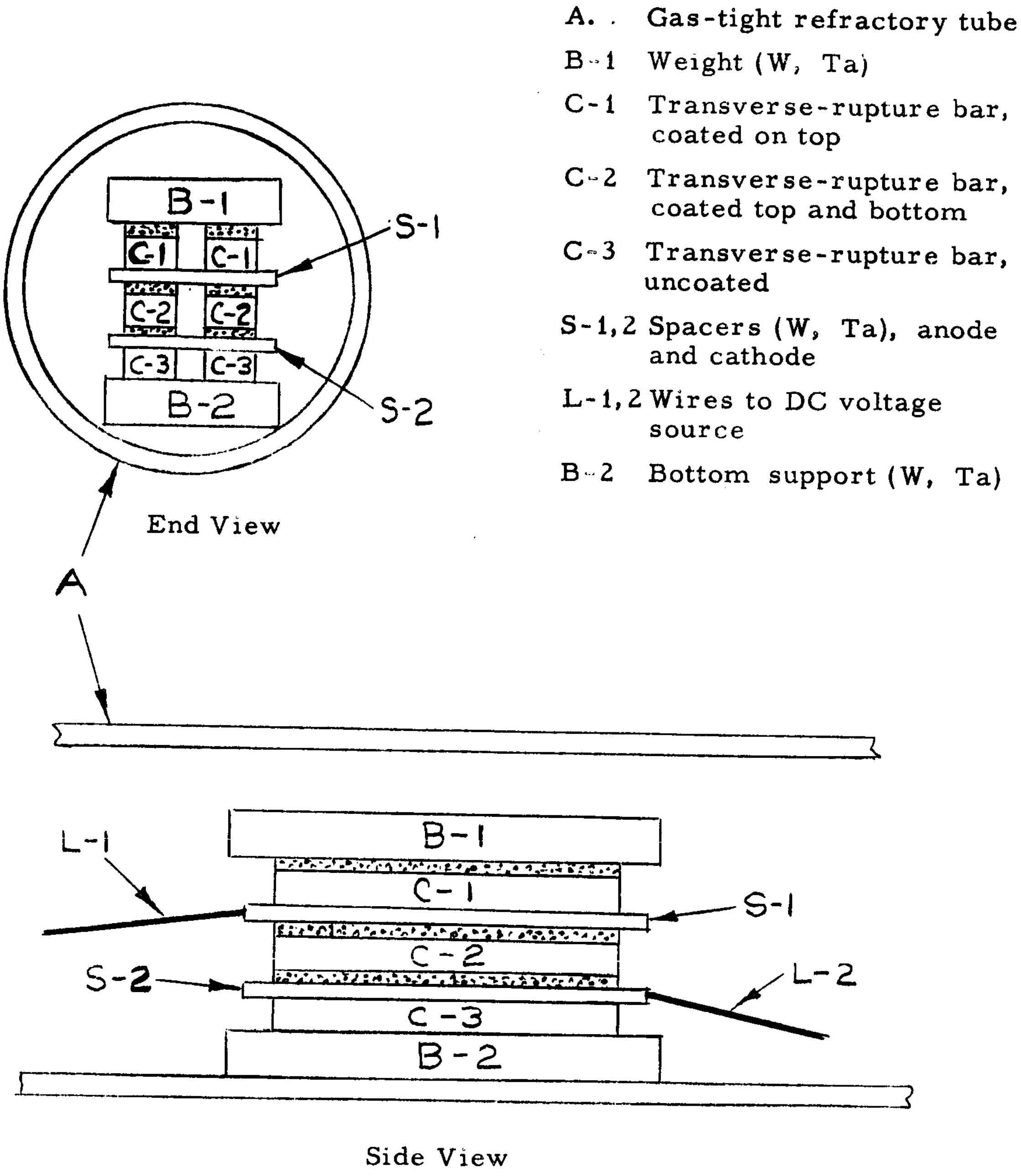


FIG. 63 - DC RESISTIVITY OF PYROLYTIC BORON NITRIDE (3/8 INCH DIAMETER BY 5/32 INCH THICK) IN HYDROGEN-ARGON. 100-hour test. Tungsten electrodes at 90 V. Molybdenum susceptor.

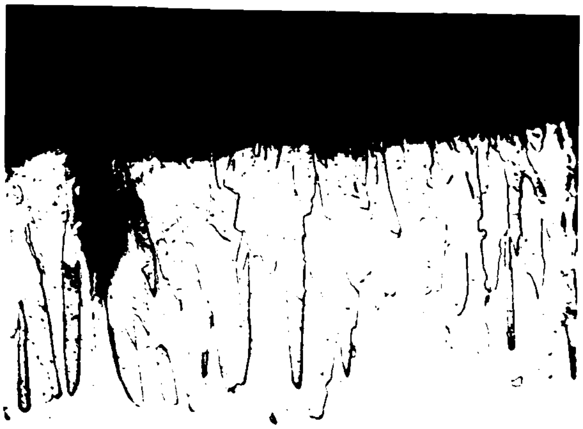


A.	Gas-tight refractory tube
B-1	Weight (W, Ta)
C-1	Transverse-rupture bar, coated on top
C-2	Transverse-rupture bar, coated top and bottom
C-3	Transverse-rupture bar, uncoated
S-1,2	Spacers (W, Ta), anode and cathode
L-1,2	Wires to DC voltage source
B-2	Bottom support (W, Ta)

End View

Side View

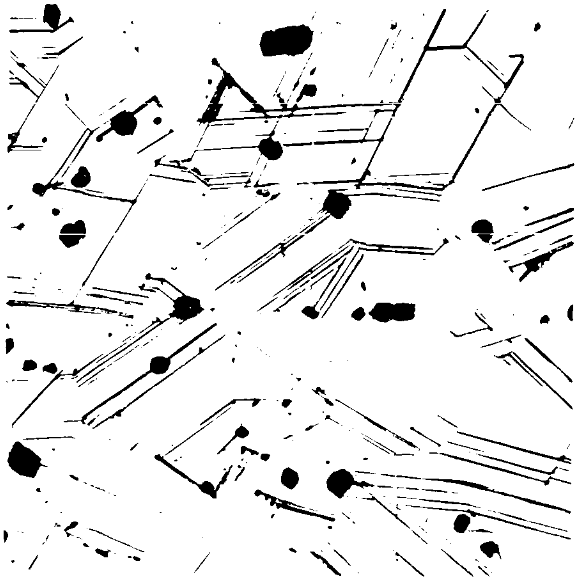
FIG. 64- SCHEMATIC SECTIONS OF ASSEMBLY FOR HEATING REFRACTORY METAL-INSULATOR SPECIMENS.



Neg. No. 26679 X200

Fig. 65

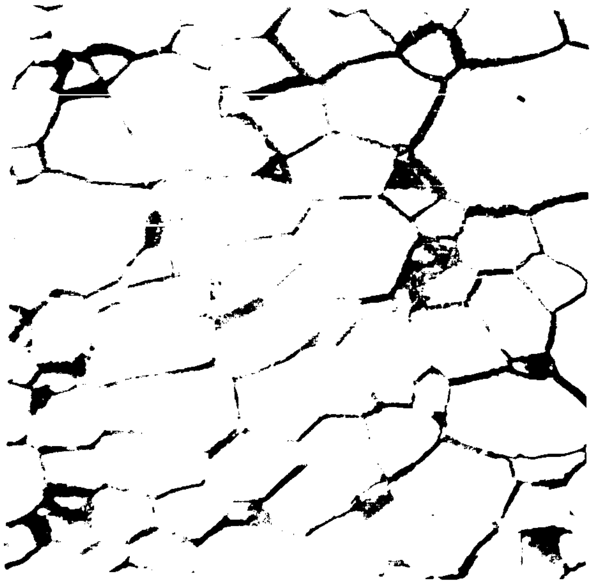
Tungsten heated in contact with BN for 98 hours at 1500°C. Columnar grains of a very hard compound, probably tungsten boride, at the tungsten surface.



Neg. No. 26680 X200

Fig. 66

Tantalum heated in contact with magnesia for 98 hours at 1500°C. A hard phase, probably an oxide, appears as globules in grain boundaries and as an oriented precipitate within the grains.



Neg. No. 26678 X200

Fig. 67

90Ta-10W alloy heated in contact with magnesia for 98 hours at 1500°C. The grain boundaries are occupied by a hard, brittle phase, probably an oxide.

Etchant: HNO_3-HF-H_2O_2-H_2O

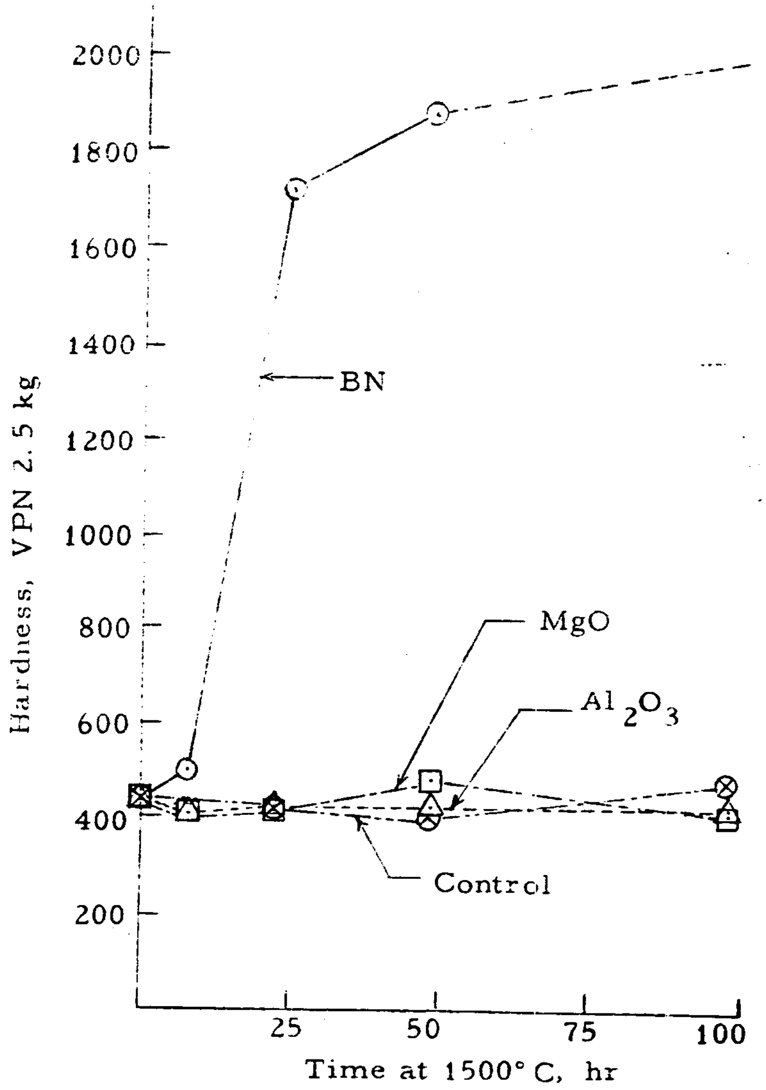


FIG. 68 - SURFACE HARDNESS DATA FOR TUNGSTEN SPECIMENS HEATED UNDER VACUUM.

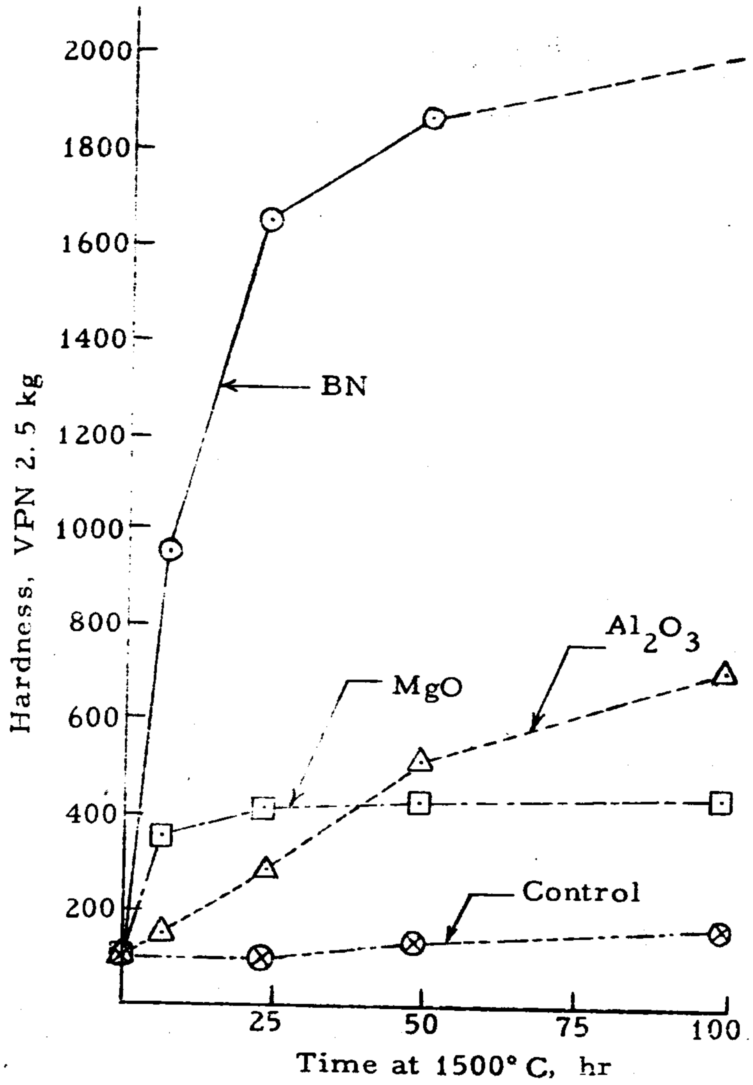


FIG. 69 - SURFACE HARDNESS DATA FOR TANTALUM SPECIMENS **HEATED** UNDER VACUUM.

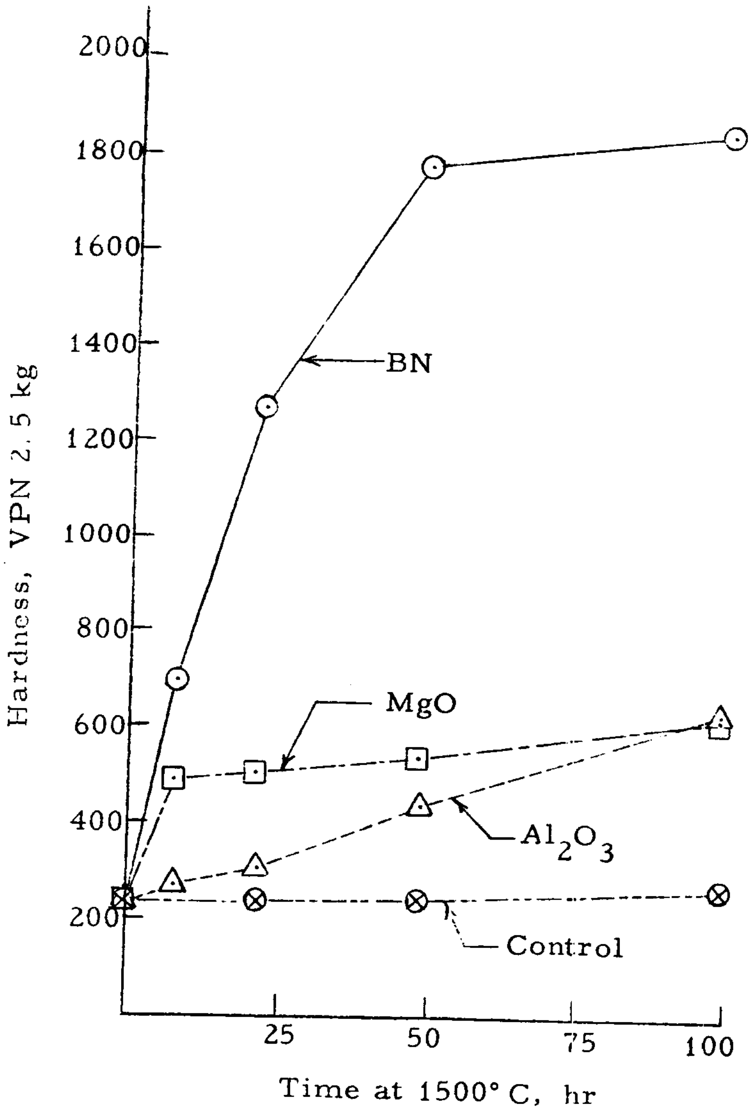


FIG. 70- . SURFACE HARDNESS DATA FOR 90Ta-10W SPECIMENS HEATED UNDER VACUUM.

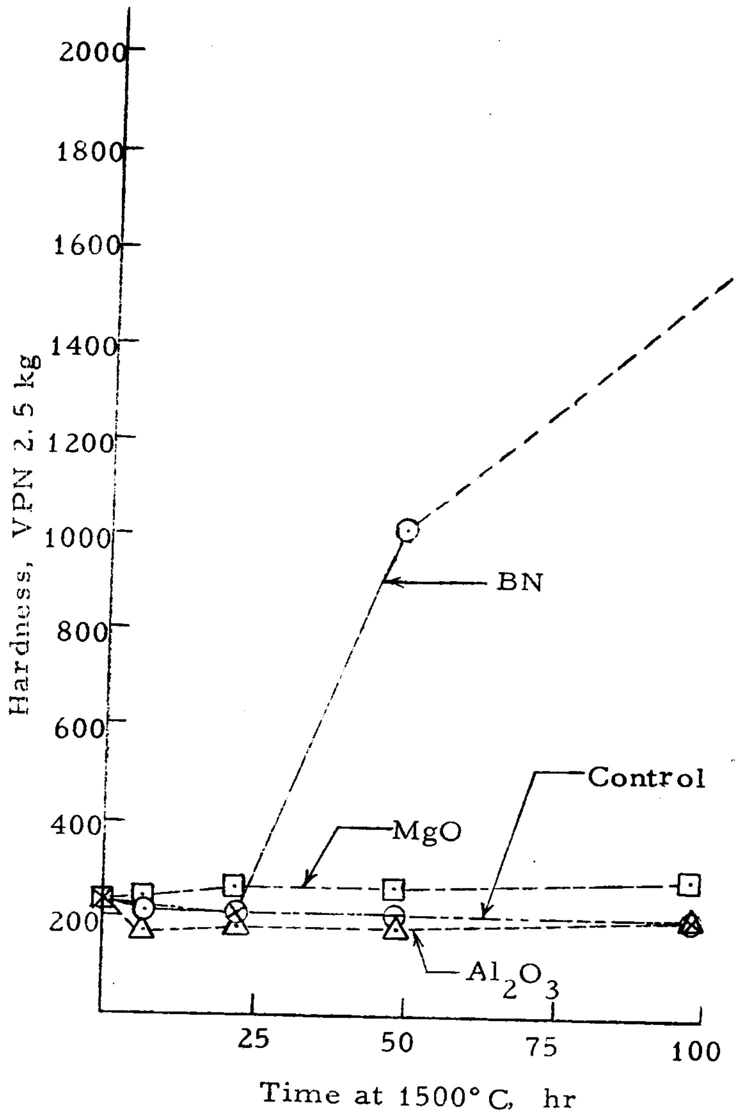


FIG. 71- SURFACE HARDNESS DATA FOR TZM SPECIMENS HEATED UNDER VACUUM.

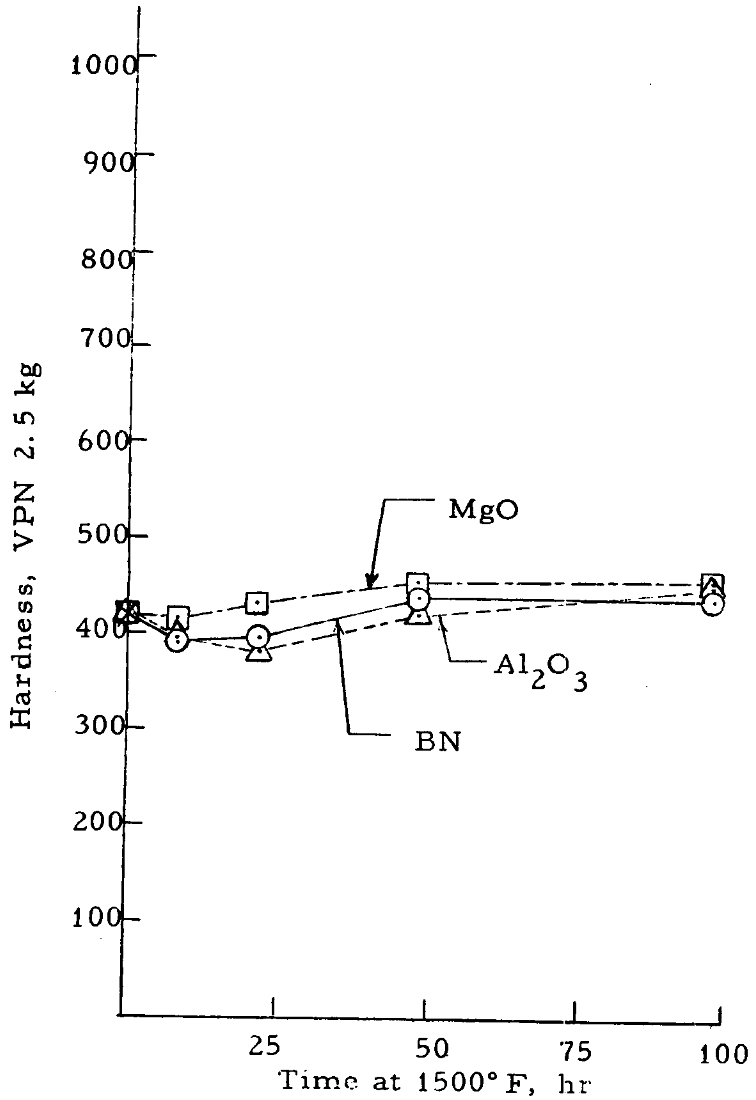


FIG. 72- CORE HARDNESS DATA FOR TUNGSTEN SPECIMENS HEATED UNDER VACUUM.

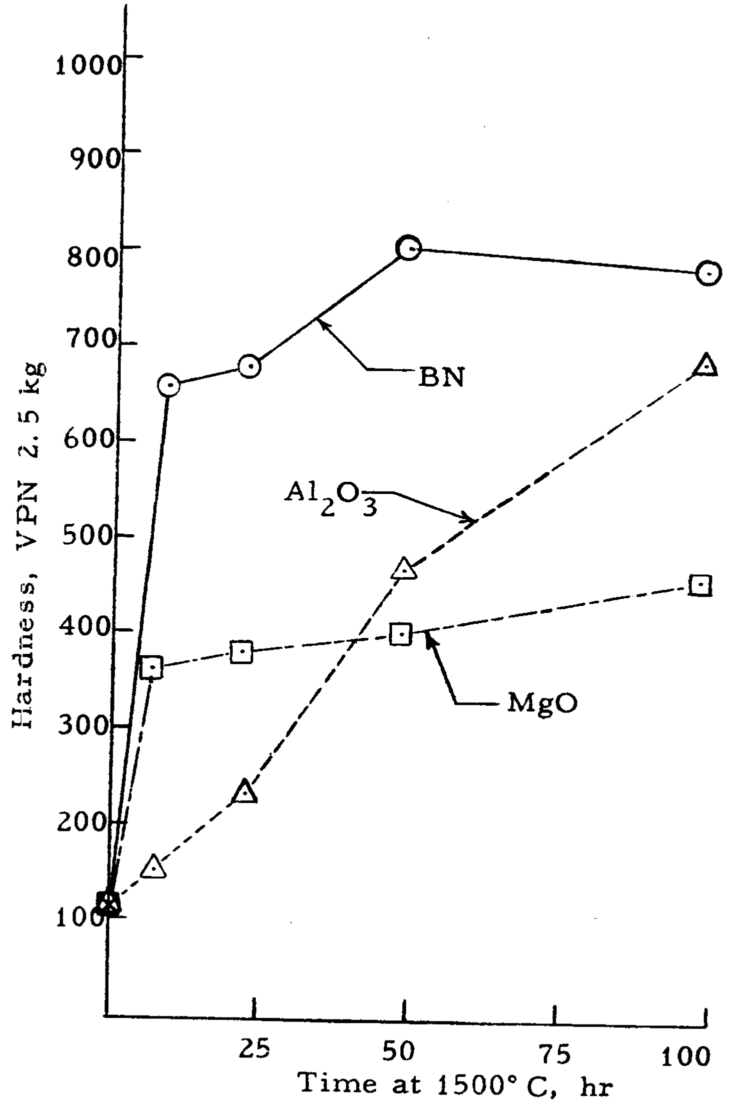


FIG. 73 - CORE HARDNESS DATA FOR TANTALUM SPECIMENS HEATED UNDER VACUUM.

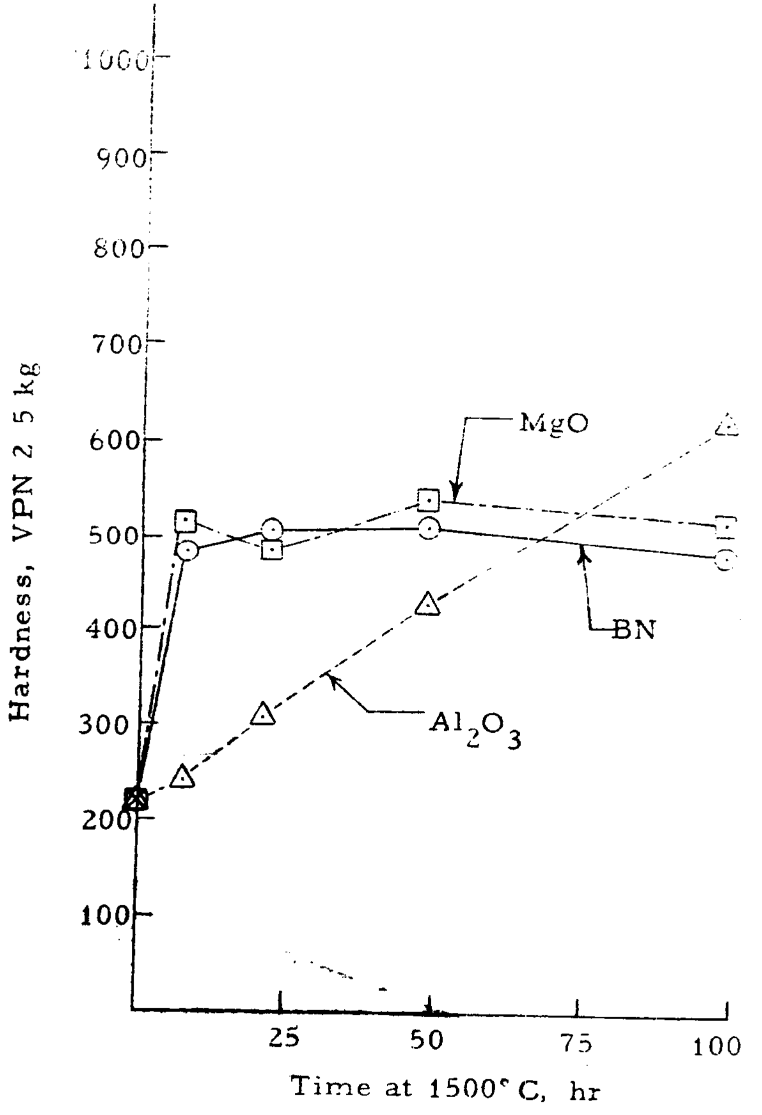


FIG. 74- CORE HARDNESS DATA FOR 90Ta-10W SPECIMENS HEATED IN VACUUM.

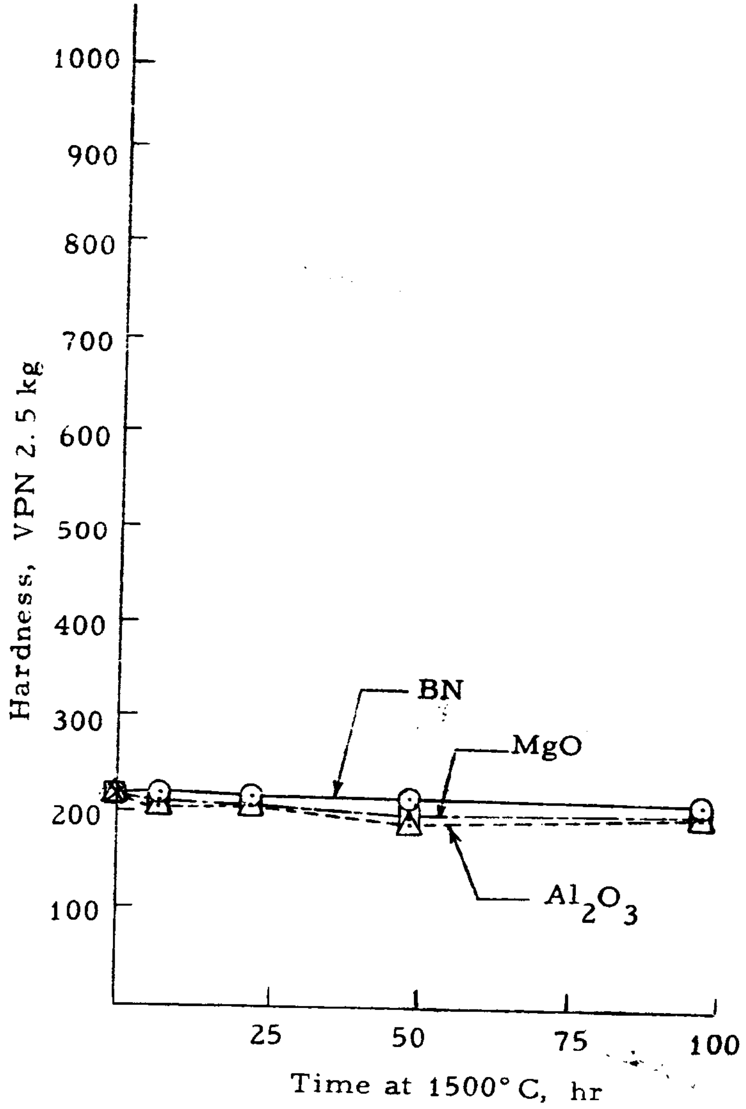


FIG. 75- CORE HARDNESS DATA FOR TZM SPECIMENS HEATED IN VACUUM.